177. Hyperconjugative Interactions in Bicyclo[2.2.1]heptane Derivatives. Effects on the *DIELS-ALDER* Reactivity of the s-*cis*-Butadiene Group of 2, 3-Dimethylidene-norbornanes

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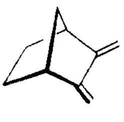
Summary. Chemical and spectroscopic properties of the s-*cis*-butadiene chromophore in 2,3-dimethylidene-norbornane can be modified without direct substitution of the diene moiety. Introduction of an etheral bridge for the $H_2C(7)$ bridge (**2**, **4**, **6**) and/or introduction of a double bond (**5**, **6**) or of an *exo*-epoxide ring (**3**,**4**) for the $H_2C(5)-H_2C(6)$ bridge causes rate decreases in the *Diels-Alder* cycloaddition with dimethyl acetylenedicarboxylate. The differences of reactivity observed between the dienes **1**–**6** are briefly discussed. Variation of the ability of the puckered cyclopentane ring of the bicyclo[2.2.1]heptane skeleton to hyperconjugate with the adjacent π-system is offered as a possible rationalization of the electronic effects.

Introduction. – 2,3-dimethylidene-bicyclo[2.2.1]heptane (**1**) is known to undergo readily *Diels-Alder* reactions with maleic anhydride [1] and dimethyl acetylenedicarboxylate (DAD) even at 0° C in the latter case. Cycloadditions to 2,3-dimethylidene-7-oxabicyclo[2.2.1]hept-5-ene (**6**) were envisaged as steps in the synthesis of oxanorbornadiene derivatives not substituted by strong electron withdrawing substituents. With this goal in mind we tried several dienophiles and found that the triene **6** reacts much more slowly than the diene **1**. High concentrations of a strong dienophile such as tetracyanoethylene (TCE) or DAD and relatively high temperature (70–130°) were necessary to generate the expected adducts. These stricking observations led us to measure the rates of *Diels-Alder* addition of DAD to **1** and **6** and to compare them with the rates of reaction of the other 2,3-dimethylidene-norbornane derivatives **2**–**5**.



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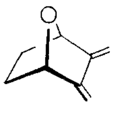

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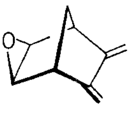

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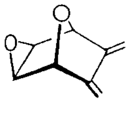

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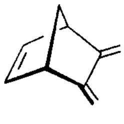

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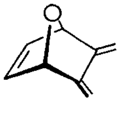

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We wish to report our preliminary results (see *Table 1*) and to discuss briefly the reactivity differences observed. Geometry changes, strain changes, steric and polar effects are probably not the most important factors that affect the reactivity of dienes **1**–**6** toward DAD. Changes in the electronic properties of the dienes must be considered as a possible source of the observed reactivity differences. A very simple

Table 1. *Summary of kinetic data of cycloadditions of dienes* **1–6** *to DAD in* CCl_4 (internal reference: toluene)

Diene:	$k^{II}_{measured}$[10^6 lmol^{-1}s^{-1}] Temperature of the measurement above [°C ± 2°; see text]				$\Delta H^{\neq}$ [kcalmol^{-1}]	$\Delta S^{\neq}$ [e.u.]	$k^{II}_{extrapolated}$ to 298 K [10^6 lmol^{-1}s^{-1}]	$k^{II}_{relative}$ (at 298 K)
1	86.5 ± 3 13.5	75 ± 1.5 12	46 ± 1.5 4.5	6.5 ± 0.2 – 15.5	12.6 ± 1.0	– 33 ± 5	220	(1.00)
2	317 ± 10 49.0	70.3 ± 3.7 29.9	25.0 ± 2.0 14.5		13.0 ± 1.0	– 34 ± 4	53	~0.24
3	191 ± 8 60.5	114 ± 3 53.2	59 ± 2 44.6	22 ± 1 31.2	14.2 ± 1.3	– 33 ± 5	14	~0.064
4	175 ± 9 68.5	75 ± 3 59.7	26 ± 1.5 42.5		14.6 ± 1.0	– 33 ± 4	7.5	~0.034
5	202 ± 10 76.0	78 ± 3 62.1	35.7 ± 1.1 52.0	18.0 ± 1.0 42.6				
	9.5 ± 0.2 36.2	2.3 ± 0.09 18.0			15.1 ± 0.8	– 33 ± 3	3.9	~0.018
6	41 ± 3 81.2	19.3 ± 1.0 70.7	4.7 ± 0.2 53.5	2.3 ± 0.2 44.5	17.0 ± 0.9	– 31 ± 3	0.36	~0.0016

MO model based on variations in the homoconjugative and hyperconjugative interactions of the s-*cis*-butadiene chromophore with the other groups in the bicyclic system is presented as a possible rationalization for these electronic effects. This MO model can also rationalize the differences in stabilities between 2-norbornyl, 2-norborn-5-enyl, 7-oxa-2-norbornyl cations and other substituted 2-norbornyl cation intermediates generated under solvolytic conditions.

Experimental part. – Dienes **1–6** were prepared according to known procedures [2] [3]^1). **1**, **2**, **3**, **5** and **6** were purified by distillation under reduced pressure; **4** was recrystallized in *n*-pentane (m.p.: 65–65.5°). Dimethyl acetylenedicarboxylate (*Fluka AG*, Buchs) was redistilled twice i.v. ("*Fischer* Spaltrohr System") and was found to contain less than 0.1% of dimethyl fumarate (GC. and ^{1}H-NMR. using the ^{13}C-satellites of DAD). Absolute CCl_4 containing a weighted amount of toluene (as internal reference) was used as solvent. The *Diels-Alder* reactions were run in the probe of a *Varian*-A6OA NMR.-instrument.

The expected adducts are the only products formed and they can be isolated in high yields for **1**, **2**, **4**, **5** and **6**. Measurements with the epoxy-diene **3** were difficult due to isomerization of the corresponding adduct formed [2]. Nevertheless, rates could be measured with acceptable accuracy at relatively low temperatures and at high concentrations of the cycloaddents. The reactions were followed for more than three half-lives (except for the very slow runs) and were found to follow pseudo-first-order rate laws when a 15 to 30 fold excess of the dienophile DAD was used. In each run, 40 to 150 concentrations measurements of the reacting diene and of the formed adduct were taken. Only the disparition of the diene could be followed in the kinetics of cycloaddition of the epoxy-diene **3** to DAD. Three different concentrations of DAD in CCl_4 were used. There was no observable effect on the rate constants k^{II} due to changes of the initial concentrations of the cycloaddents and due to changes in their initial concentration ratios.

Great care in stabilizing the temperature of the NMR. probe was taken. Measurement conditions (length of the NMR. tube, volume of the investigated solutions, pressure and flow of the cooling or heating nitrogen, spinning rate of the tube, *etc.*) were set rigourously identical in all kinetic runs. Pseudofirst-order rate-constants k'^{I} were measured at different temperatures. *Arrhenius* plot of the measured values of $k^{II} = k'^{I}/[DAD]$ and T allowed the evaluation of activation parameters. The rate constants at 298 K were obtained by extrapolation, using $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values. The errors reported on k^{II} (see *Table 1*) are the standard deviations on the measured k'^{I} plus the estimated errors on the DAD concentrations. The largest source of inaccuracy is the temperature measurement (± 2°) of the mixture under investigation. This error is believed larger than the temperature fluctuations of the NMR. probe (the temperature before and after the kinetics were found to stay within a range $< 0.6°$). Thus, the standard deviations calculated on the activation parameters do not represent the actual errors. Our data must be considered as preliminary results; they have presently an indicative value only. A large part of the error on the temperature measurement is, however, a systematic error which has the same sign and probably

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^{1}) We wish to thank Prof. Dr. *W.R. Roth* for a detailed prescription of the preparation of 2,3-(dihydroxymethyl)-7-oxanorborn-5-ene, starting material in the synthesis of **6** [4].

the same magnetude in all the reactions studied in our conditions. For that reason, we feel confident in discussing the observed reactivity differences between the cycloadditions of **1**–**6** to DAD (see *Table 1*).

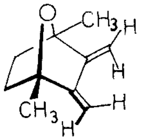
Results. Our kinetic data on the cycloadditions of dienes **1**–**6** to DMA are summarized in *Table 1*. Activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ were determined and were used to extrapolate the second-order rate constants to 25°. For all the reactions investigated, the $\Delta S^{\ddagger}$ terms are found to have comparable values; therefore, the enthalpy term $\Delta H^{\ddagger}$ is responsible for differentiating the reactivity of dienes **1**–**6** toward DMA.

The comparison of the rate constants of cycloadditions of DMA to 2,3-dimethylidene-norbornane (**1**) and 2,3-dimethylidene-7-oxanorbornane (**2**) shows a retardation effect of about 4 at 25° due to the introduction of an oxygen bridge O(7) for the $H_2C(7)$ bridge. Similar rate retardation effects are found for the *exo*-5,6-epoxy derivatives **4** vs. **3** and the trienes **6** *vs.* **5** (retardation effect of about 2 and, respectively, about 10). Comparison of the rates of addition of DAD to **1** and **3** shows that the *exo*-5,6-epoxide ring introduces a rate retardation of about 15. A similar effect is found in the 7-oxanorbornane derivatives **4** *vs.* **2**. The 2,3-dimethylidene-norborn-5-ene (**5**) and the 2,3-dimethylidene-7-oxanorborn-5-ene (**6**) are much less reactive toward DAD than the corresponding dienes **1** and **2**. The endocyclic double in **5** and **6** introduces a rate retardation effect of about 56 and, respectively, about 147. Our measurements indicate that the reactivity of the s-*cis*-butadiene group in 2,3-dimethylidene-norbornane can be modified without direct substitution of the diene moiety. Remote substituent or group effects are observed by introducing non-conjugated chromophores such as an endocyclic double bond between C(5) and C(6), an *exo*-5,6-epoxide ring and/or an etheral bridge O(7) in the bicyclic skeleton. The effects are multiplicative on the rate constants in a first approximation. The largest retardation effect is introduced by the endocyclic double bond.

Discussion. – Several phenomena can be invoked a priori to explain our observations. Among them are: (a) geometry changes of the diene moiety in the starting compounds **1**–**6** due to modifications of geometry and ring strain of the bicyclic skeleton; (b) steric hindrance changes due to modified gauche interactions between the cycloaddents in the transiton state; (c) variations in the electrostatic interactions between the cycloaddents themselves, between the solvent and the cycloaddents and between the solvent and the transition states; (d) differences in electronic properties of the s-*cis*-butadiene group in **1**–**6** due to through-space (homoconjugation) and through-bond (hyperconjugation) interactions [5] between the non-conjugated chromophores.

Estimations of heats of *Diels-Alder* reactions from standard enthalpies of formation in the gas phase of unsubstituted dienes, ethylene and the corresponding adducts are found to agree quite nicely with the measured heat of reaction in the condensed phase for substituted, polar cycloaddents [6]. The experimental heat of formation of dienes **1**–**6**, DAD and their corresponding adducts are not known. An estimation of the heat of reaction of **1**–**6** with DAD is given by comparison with analogous cycloaddition of butadiene to acetylene for which an exothermicity of 53–56 $kcal mol^{-1}$ is found in the gas phase [7]. The 1,4-cyclohexadiene ring annelated to the norbornane system introduces a strain increase which is estimated to be 7–12 kcalmol^{-1} [2]). Therefore, an exothermicity of 40–50 kcalmol^{-1} can be estimated for the *Diels-Alder* cycloadditions of DAD to the dienes **1**–**6**. This corresponds to about three times the observed activation enthalpies. Assuming a one-step mechanism [9] and according to the *Bell-Evans-Polanyi* principle, the properties of the starting dienes and of the dienophile can be used to approximate the characteristics of the transition state of the *Diels-Alder* cycloadditions of **1**–**6** with DAD.

Molecular models show minute changes in geometry of the diene moiety in **1**–**6**. Our modifications of the bicyclic skeleton are expected to introduce changes in ring strain. The introduction of an etheral bridge O(7) for the $H_2C(7)$ bridge is known to remove some strain from the bicyclo[2.2.1]heptane skeleton [10] whereas replacing the C(5), C(6) ethano bridge by a double bond or by an epoxide ring raises it [11] [7]. The data reported in table 1 show that the effects observed on the reactivity of the dienes **1**–**6** do not correlate with the ring strain. Steric hindrance (gauche interactions) between the cycloaddents in the transition state are minimized by using an acetylenic dienophile such as DAD and because there is no substituent on the methylidene carbon-atoms of the dienes. In the 1,4-dimethyl-2,3-dimethylidene-7-oxanorbornane (**7**), gauche interactions between the bridgehead methyl substituents



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and the methylidene hydrogen-atoms are expected to introduce some geometry distortion into the s-*cis*-butadiene chromophore. Kinetic measurements of *Diels-Alder* additions of **7** and **2** to DAD (by ^{1}H-NMR.) and to tetracyanoethylene by competitive reaction technique (GC. analysis) showed that these two dienes have very similar reactivities toward strong dienophiles. Differences in solvation energies between **1**–**6** and their corresponding transition states of reaction with DAD can play a role; nevertheless, it has been found in several instances that the *Diels-Alder* reactions with strong dienophiles are solvent insensitive [12]. Changes in dipole-dipole interaction between the cycloaddents can affect the reactivity of dienes **1**–**6**. A polar substituent such as the *exo*-5,6-epoxide ring or the etheral bridge O(7) modifies the dipole moment of the 2,3-dimethylidene-norbornane. If the polar substituent does not modify the π-electron density in the diene moiety (decrease or increase of atomic coefficients on the methylidene carbon-atoms in the occupied π-orbitals) the effects due to changes in dipole-dipole interactions between the dienes and the dienophile will be minimized due to the symmetry of the reactants and because the 'linear' DAD attacks the dienes 'perpendicularly' to their mirror plane[3]).

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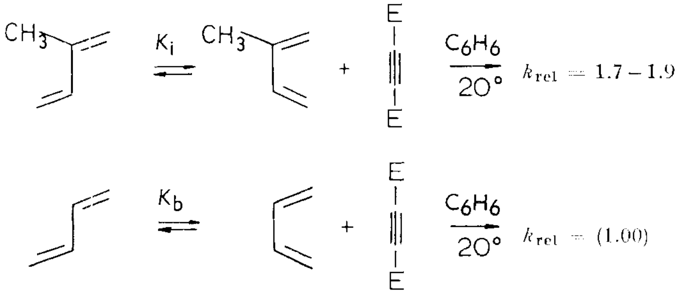
[2]) 8 kcalmol^{-1} of strain is found in 1,4-dihydronaphtalene [7]. Annelation of norbornane by a 2,3-cyclopentane ring introduces a strain increase of 5–7 kcalmol^{-1} [8]. The same number of sp^2 carbon atoms are present in the bicyclic skeleton of the starting dienes **1**–**6** and in their corresponding adducts.

[3]) Preliminary results with exo-5-hydroxy- and exo-5,6-dihydroxy-2,3-dimethylidene-norbornanes have shown that the polar hydroxyl substituents in C(5), C(6) do not modify, apparently, the reactivity of the diene group in these compounds relative to the parent diene **1** [13].

From the foregoing assumptions and our results with **7** we suggest that geometry changes, strain changes and steric effects are probably not the most important factors that differentiate the reactivities of dienes **1**–**6** toward DAD. Although they cannot be neglected *a priori*, we think that changes in electronic properties of the s-*cis*-butadiene chromophores of **1**–**6** must also be considered as a possible source of the observed effects.

The *Diels-Alder* rate retardation effects introduced by our modifications of the bicyclic skeleton of 2,3-dimethylidene-norbornanes are much larger than the difference in reactivity between isoprene and butadiene toward DAD [14].



$K_i \gg K_b$ [39] E = $COOCH_3$

Both perturbation (PMO) and frontier molecular orbital (FMO) theories have been applied to the *Diels-Alder* reaction [15]. It has been shown that the FMO approach can predict the difference in reactivity quantitatively from the interactions between the frontier MO's of the cycloaddents when the other factors are constant, or are linearly related to the frontier MO-energies. In reactions with electron-deficient dienophile such as DAD, the diene HOMO-dienophile LUMO interaction is the strongest and determine the reactivity. If the influence of the diene LUMO-dienophile HOMO [16] as well as extra-frontier orbital interactions can be considered negligible (that is not true *a priori*), the energy and the shape (atomic coefficients) of the HOMO of the diene **1**–**6** should make possible the prediction of their relative reactivities toward a strong dienophile. Assuming the non-electronic effects to be unsignificant, the higher the energy of the HOMO of the diene and its atomic coefficients on the methylidene centres, the more rapidly it will react with DAD.

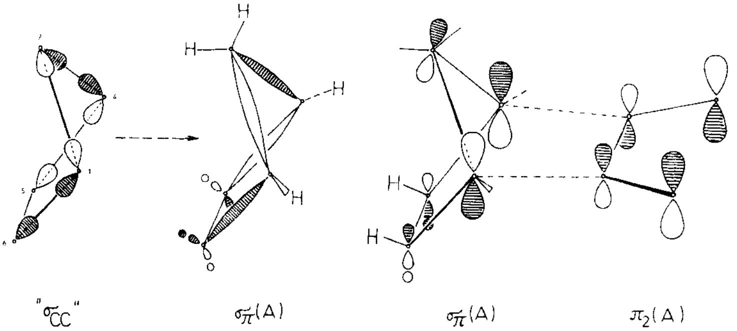


Fig. 1. *Simplified representation of the localized HOMO-$\sigma_\pi(A)$ of the puckered cyclopentane ring and its hyperconjugative interaction with the localized HOMO-$\pi_2(A)$ of the* s-cis-*butadiene chromophore*

In a first approximation, the properties of the 2,3-dimethylidene-norbornane (**1**) corresponds to those of the unsubstituted s-*cis*-butadiene perturbed by an adjacent puckered cyclopentane ring. In particular, the interaction between the localized orbitals $\sigma_\pi(A)$ (the HOMO of the bent cyclopentane ring [17] and $\pi_2(A)$ (the HOMO of the s-*cis*-butadiene group)) generates semi-localized linear combinations $\varphi_+ = a \cdot \sigma_\pi(A) + b \cdot \pi_2(A)$, with $a > b$, and $\varphi_- = b' \cdot \pi_2(A) - a' \cdot \sigma_\pi(A)$, with $b' > a'$. The latter combination gives a first approximation to the HOMO of the diene **1**; its energy is higher than that of the localized orbital $\pi_2(A)$. Similar interaction occurs between localized unoccupied MO's and generates a LUMO for the diene **1** whose energy is probably lower than that of the localized LUMO $\pi_3^*(S)$ of the unsubstituted s-*cis*-butadiene chromophore. This is experimentally confirmed by the comparison of the UV. absorption spectrum of **1** with those of simpler dienes [2], assuming the singlet excitation energies of these olefins to correlate linearly with their LUMO-HOMO energy differences [18]. Interaction between the localized, lower-lying subjacent orbitals $\sigma_\pi(S)$ of the bent cyclopentane ring and $\pi_1(S)$ of the diene moiety is also expected to generate a semi-localized combination $c \cdot \pi_1(S) - d \cdot \sigma_\pi(S)$, with $c > d$, that is higher lying than the localized MO $\pi_1(S)$[4].

The localized HOMO $\sigma_\pi(A)$ of the puckered cyclopentane ring in the bicyclo[2.2.1]heptane system is represented in *Fig. 1*. It can be viewed as a linear combination of $sp^3(C)$ and $s(H)$ atomic orbitals: a combination of 'σ_{CC}' (the HOMO of a 10 carbon atom electron system having 4 nodes) with CH bonds. An equivalent HOMO of the bent cyclopentane can be generated using p and $\sigma_\pi(CH_2)$ orbitals [20]. Phase inversion (defining the π-sign of $\sigma_\pi(A)$) is implied at centres C(1)/C(4) of the bicyclic system. These centres are, in a first approximation, in the π-plane of the diene moiety. Since $H_{7syn,7anti}$ are in the mirror plane of **1** and since the bridgehead hydrogen atoms at C(1)/C(4) are located close to the pseudo-symmetry plane π, there will be very little or no electron density spread over these hydrogen centres by $\sigma_\pi(A)$ (little admixture of σ_{C_1-H} and σ_{C_4-H} and no admixture of $\sigma_{C_{7a}-H}$ and $\sigma_{C_{7s}-H}$ into 'σ_{C-C}' for reason of symmetry). Furthermore, due to the antibonding character between C(5) and C(6), enlarged coefficients are built up on C(1)/C(4) for $\sigma_\pi(A)$. This point is of importance since the larger the coefficients on C(1)/C(4), the greater will be the overlap, and consequently, the interaction of $\sigma_\pi(A)$ with the adjacent $\pi_2(A)$ of the s-*cis*-butadiene. The subjacent MO's of the cyclopentane ring, as well as its empty MO's, will have little effect on $\pi_2(A)$ of the diene when these two groups interact together, for reasons of symmetry and/or due to the large energy gap between the orbitals involved.

When $H_2C(7)$ in **1** is replaced by an etheral bridge, the energy of the localized MO $\sigma_\pi(A)$ is lowered and the atomic coefficients on C(1)/C(4) are decreased due to the inductive effect of the oxygen atom. Similar effects are expected also in the subjacent occupied localized MO's of the bent five-membered ring. The n-orbitals of the oxygen atom in the 7-oxa-norbornane derivatives **2**, **4** and **6** cannot interact with the localized molecular orbital $\pi_2(A)$ of the diene for reason of symmetry. Therefore, the introduction of an oxygen bridge O(7) for the $H_2C(7)$ brigde will stabilize the

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[4] This is true when the localized MO $\sigma_\pi(S)$ of the σ_{CC} framework lies below the localized MO $\pi_1(S)$ of the s-*cis*-butadiene. PES. data seem to agree with this hypothesis [19].

HOMO of the diene due to a diminished hyperconjugative destabilization by the puckered five-membered ring.

For reason of symmetry, the localized frontier orbitals π_2(A) and π_3^*(S) of the s-*cis*-butadiene group cannot interact with the localized frontier orbitals π(S) and, respectively, π^*(A) of the endocyclic double bond C(5),C(6) in **5** and **6**. Through-space interactions (homoconjugation) between π_2(A) and the unoccupied π^*(A), and between π_3^*(S) and π(S) are possible. Nevertheless, due to the large distance separating the two interacting systems, and due to the very large energy gap between the localized MO involved, these interactions are expected to be very small. It can become important if a through-bond mechanism is operative [5]. The properties of the 2,3-dimethylidene-norborn-5-ene are those of the s-*cis*-butadiene perturbed by the bent cyclopentene ring whose localized HOMO σ_π'(A) can be envisionned as arising from the admixture of some π^*(A) of the double bond into a 'σ'_{C-C}(A)' MO (linear combination of 3 sp^3(C) and 2 sp^2(C) atomic orbitals) of the bent cyclopentene ring (see *Fig. 2a*). This combination generates a localized HOMO for the puckered cyclopentene ring that is lower lying than the localized HOMO of the saturated system (stabilization of the σ MO's through inductive effect of the double bond [21]). Thus, the hyperconjugative destabilization of π_2(A) is expected to be smaller in the trienes **5** and **6** than in the dienes **1** and **2** due to the stabilization effect introduced by the endocyclic double bond between C(5) and C(6).

The symmetry of the localized MO's π_2(A) and π_3^*(S) of the s-*cis*-butadiene group in the *exo*-5,6-epoxy derivatives **3** and **4** forbids any through-space and/or through-bond interactions with the localized HOMO e(S), respectively, with the localized LUMO e*(A) of the epoxide ring. The effect of the oxirane group on the σ-skeleton is similar to that introduced by the C(5),C(6) double bond. The localized LUMO e*(A) stabilizes the localized HOMO of the bent cyclopentane ring and leads to a diminished hyperconjugative destabilization of the HOMO of the diene (see Fig. 2b).

Our rudimentary MO considerations suggest that the introduction of an oxygen bridge O(7) for the H_2C(7) bridge, the introduction of a double bond or of an *exo*-epoxide ring for the C(5),C(6) ethano bridge in 2,3-dimethylidene-norbornane causes a decrease in the energy of the HOMO of the diene. Assuming the PMO arguments to be applicable in the case of the cycloadditions of dienes **1**–**6**, one predicts the parent

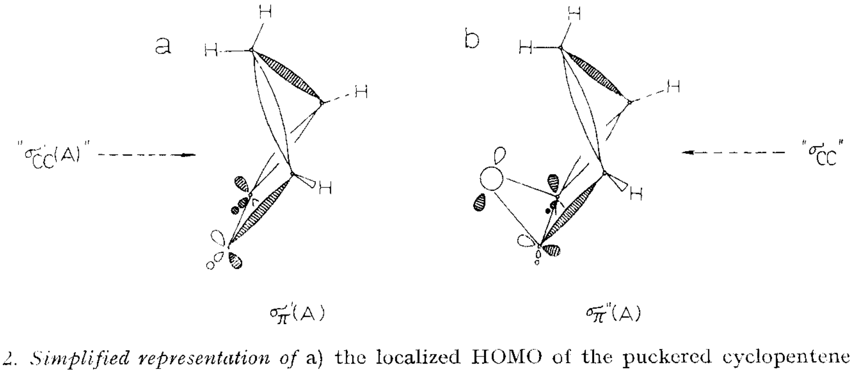

Fig. 2. *Simplified representation of* a) the localized HOMO of the puckered cyclopentene ring: σ'_π(A) and of b) the "*syn*" epoxy-cyclopentane ring: σ''_π(A)

diene **1** to react the fastest with a strong dienophile, whereas, the epoxy-diene **4** and the triene **6** are predicted to react the most slowly.

Our kinetic results with DAD are in complete agreement with these predictions[5]).

We have limited, thus far, our MO considerations to changes in energy of the HOMO of dienes **1**–**6**. The *Diels-Alder* reactivity depends also upon the relative size of the atomic coefficients in the HOMO of the dienes. Furthermore, the LUMO(diene – HOMO(dienophile) interactions may also play a role.

Hypsochromic shifts are observed in the UV. absorption spectra for the V ← N transition of the s-*cis*-butadiene chromophore (see *Table 2*) when $H_2C(7)$ in **1**, **3** and **5** is replaced by an etheral bridge (**2**, **4** and **6**) and/or when the C(5),C(6) ethano bridge is replaced by an *exo*-epoxide ring (compare **3**, **4** with **1**, **2**) or by an ethylene group (compare **5**, **6** with **1**, **2**). The effects are additive in a first approximation. Methyl substituents in C(1)/C(4) do not perturb the UV. properties of the diene (compare **7** with **2** [2]). Furthermore, the effects found **1**–**6** due to the structural modifications of the bicyclic system are not observed in monocyclic derivatives [2]. If the singlet excitation energies correlate linearly with the LUMO-HOMO energy differences and/or with the changes of the atomic coefficients in these orbitals [18], these observations indicate that the changes in the LUMO(diene)-HOMO(dienophile) interactions between **1**–**6** and DAD are related to the HOMO(diene)-LUMO(dienophile) interactions in a way that reinforces the dominant effect of these latter interactions on the *Diels-Alder* reactivity.

The semi-localized HOMO $\varphi_- = b' \cdot \pi_2(A) - a' \cdot \sigma_\pi(A)$ is a first approximation to the HOMO of diene **1**. A second approximation would be to include some interactions with the empty MO's. For reason of symmetry, the largest contribution arises from the localized $\pi_4^*(A)$ of the diene group. This interaction leads to a slightly stabilized HOMO whose atomic coefficients have increased on the methylidene carbons and decreased on the quaternary centres of the s-*cis*-butadiene chromophore. The same type of polarization of the π electrons is expected also for the subjacent occupied MO $c \cdot \pi_1(S) - d \cdot \sigma_\pi(S)$. Thus, hyperconjugative destabilization of the HOMO in dienes **1**–**6** will accelerate the *Diels-Alder* additions to a strong dienophile because of a smaller energy gap between the LUMO(dienophile) and HOMO(diene) and because of increased overlap between these orbitals. At the limit, it is possible that the HOMO energies of dienes **1**–**6** are not modified or vary in a very narrow range; the hyperconjugation would affect only the shape of these MO's due to changes in energy and coefficients of the unoccupied orbitals.

^{13}C-chemical shifts of the olefinic carbons in **1**–**6** are reported in *Table 2*. One observes that the energy of V ← N transition of the s-*cis*-butadiene chromophore correlates with the chemical shifts of the methylidene carbons, with the chemical shifts of the quaternary carbon atoms and with their differences. According to the *Karplus & Pople*'s theory of ^{13}C-chemical shift [22] and assuming the paramagnetic term to be dominant in determining the $\delta(^{13}C)$ of the olefinic carbons in **1**–**6**, our spectral observations support the hypothesis of a 'linear' π-electron density change

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[5]) Preliminary results obtained by competitive kinetic measurements of *Diels-Alder* additions with tetracyanoethylene at 25° have shown that the reactivity differences between **1**–**6** are larger than those found in the cycloadditions with DAD.

Table 2. *UV and ^{13}C-NMR. characteristics of dienes* **1–6**

Dienes	**1**	**2**	**5**	**3**	**4**	**6**
λ_{max} (in solution[a]) [nm]	248	242	241	239	235	233
λ_{max} (in gas phase; 20°) [nm]	242	236.5	235.5	234.5	232	228.5
$\Delta E(V \leftarrow N)$ [cm^{-1}]	41320	42280	42460	42640	43100	43760
$\delta_{C2,3}$ [ppm][b]	152.1	148.1	148.4	147	144	143
$\delta_{CH2=C2,3}$	99.3	99.8	101.1	103.3	104.5	102.3
$\delta_{(C quat.)} - \delta_{(CH2)}$	52.8	48.3	47.3	43.7	39.5	40.7

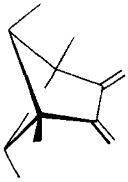
[a] Same values for λ_{max} are observed in isooctane and 95% ethanol; the V←N transition of dienes **1–6** is split into three bands due to vibrationnal coupling. The central band is generally the highest in intensity and it is reported here.

[b] In CDCl$_3$, TMS as internal standard (δ_{TMS} = 0.0 ppm).

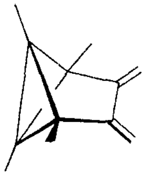
with the change of energy and shapes of the frontier and extrafrontier MO's of the dienes in the way suggested by our simple MO model.

Our kinetic and spectral data do not prove that non-electronic effects play only secondary role in differentiating the *Diels-Alder* reactivity of dienes **1–6**. Nevertheless, we think that they are consistent with our simple MO model rationalizing the electronic properties of these compounds[6]).

Recently, the difference in reactivity of dienes **8** and **9** toward TCE has been rationalized in terms of different interactions between localized orbitals of the s-*cis*-butadiene chromophore and the puckered cyclobutane ring in **8** and bicyclobutane in **9** [25]. In these two tetramethyl substituted derivatives geometry changes (due to ring strain and modification of methyl-methylidene gauche interactions) are expected to be larger than in our dienes **1–6**. Nevertheless, the geometrical effects on the reactivity of **8** and **9** have been estimated to be small compared with the electronic effects.



8



9

Interactions of the localized HOMO σ_π(A) (and the subjacent MO's) of a puckered cyclopentane group with an adjacent empty p orbital, as one can find it in 2-norbornyl cations, leads to a stabilization of these species. Our simple MO model predicts that the unsubstituted, classical 2-norbornyl cation is more stabilized through

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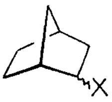
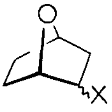
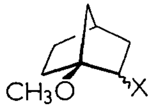
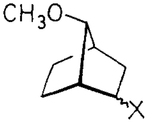
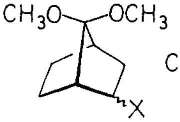
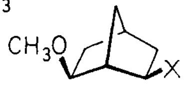
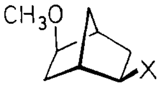
[6]) The reactivity difference noted recently by *Butler & Snow* [23] between 2,3-dimethylidene-norbornane derivatives and 2,3-dimethylidene-bicyclo[2.2.2]octane can be explained by a stronger hyperconjugative destabilization of the HOMO (by the σ(AA) localized HOMO of the boat cyclohexane ring [24]) in this latter diene than in other 2,3-dimethylidene-norbornanes, were substitution of the bicyclic skeleton introduces inductive effects that stabilize σ_π(A) and reduces its coefficients on C(1)/C(4).

hyperconjugation[7]) than 2-norborn-5-enyl [29] and 7-oxa-2-norbornyl cation [30]. Solvolysis data (see *Table 3*) involving these cationic intermediates are consistent with these predictions[8]).

Due to its inductive effect, a methoxy stabilizes the localized HOMO $\sigma_\pi(A)$ and the subjacent MO's of the puckered cyclopentane ring. This leads to rate retardation effects in the solvolysis of methoxy substituted 2-norbornyl esters (see *Table 3*). These solvolysis retardation effects could also be explained by a dipole-dipole destabilization (through-space interaction) of the forming carbocation intermediate. However, such classical electrostatic effects cannot explain the greater retardation effect found in the acetolysis of *exo*-5-methoxy-2-norbornyl tosylate than in the acetolysis of *exo*-6-methoxy-2-norbornyl tosylate relative to the unsubstituted

Table 3. *Summary of kinetic data on solvolysis of secondary 2-norbornyl derivatives* (relative titrimetric rates)

				
X = Cl[a])	*exo*: 420000 *endo*: 6000	*exo*: 211 [30] *endo*: (1.00)		
X = OBs[b])	*exo*: 350 *endo*: (1.00)		($k_{\mathrm{rel,\,polarimetric}}$: 1600) [31] 129[8]) [32] 0.016	279 [31] 0.0285
X = OTs[b])	*exo*: 280 [33] *endo*: (1.00)			
				
X = OTs[b])	*exo*: 24 [34] *endo*: 0.36	1.1 [34] 0.03	39 [35]	3.9 [35

[a]) in 80% aq. EtOH at 85°; [b]) in AcOH/NaOAc at 25°.

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[7]) This vertical stabilization affects the solvolysis rates of both *exo*- and *endo*-2-norbornyl derivatives. Steric effects, certainly, play also a role in differentiating the reactivity of *exo*- and *endo*-isomers [26]. Since the localized HOMO $\sigma_\pi(A)$ and the subjacent MO $\sigma_\pi(S)$ of the puckered cyclopentane ring are in fact not symmetric relative to the π-plane of the positively charged centre C(2), one expects the hyperconjugative stabilization to be responsible, in part, for the *exo/endo* selectivity (see kinetic data on solvolysis of 1-substituted 2-norbornyl derivatives [27]). Increased hyperconjugative stabilization due to the presence of excess p character in C–C bonds had already been suggested as being responsible for the observed abnormally high rate of *Friedel-Crafts* benzoylation of the norbornyl-benzenes and for the accelerated rates of solvolysis of 2-norbornyl esters [28].

[8]) Solvolysis of secondary *exo*-2-norborn-5-enyl esters are accelerated by a factor of about 20 due to π-participation [36]. Taking into account this participation (through-space stabilization of the cationic transition state), the retardation effect on the titrimetric rate of solvolysis of 2-norborn-5-enyl derivatives relative to the satured 2-norbornyl esters would be about 40. Strain effects might also play a role in differentiating the reactivities of these esters.

derivative [35]. These observations might be explained by invoking the polarisability (through-bond interaction) of the 'ribbon' localized HOMO σ_π(A) and the subjacent MO's of the bent cyclopentane ring in the bicyclo[2.2.1]heptane systems. The atomic coefficient in C(1) of σ_π(A) is expected to be decreased to a greater extent by the inductive effect of the $CH_3O–C_{(5)}$ group than by the inductive effect of the $CH_3O–C_{(6)}$ group.

Conclusion. – Differences in electronic properties of dienes **1–6** might be responsible for the reactivity differences observed in the *Diels-Alder* additions of these compounds to a strong dienophile such as dimethyl acetylenedicarboxylate (DAD). Variation of the ability of the puckered five-membered ring C(1)–C(7)–C(4)–C(5)–C(6) of the bicyclo[2.2.1]heptane systems to hyperconjugate with the adjacent π-system in C(2),C(3) is proposed as a possible rationalization for the observed effects. These hyperconjugative interactions modify the energies and/or the shape of the frontier orbitals for the dienes. They involve the localized frontier orbitals of the puckered cyclopentane ring whose energies and atomic coefficients in C(1)/C(4) can be modified by structural modification and substitution of the norbornane skeleton. The largest interaction occurs probably between the localized HOMO σ_π(A) of the bent cyclopentane ring (which has 'enlarged' coefficients on C(1)/C(4)) and the localized HOMO π_2(A) of the s-*cis*-butadiene chromophore. In 2-norbornyl cations, the largest interaction will occur between the localized σ_π(A) and the empty p orbital of the cation. That simple MO model can rationalize kinetic data on solvolysis of 2-norbornyl esters and substituted derivatives without invoking non-classical, bridged carbocation intermediates. It suggests also that a puckered cyclopentane ring can, like a cyclopropane ring [37], a cyclobutane ring [17] [19] [38] or a bent cyclohexane ring [24], participate in hyperconjugative stabilization or destabilization with an adjacent π-system.

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