42. Participation of Non-Conjugated Double Bonds in *Diels-Alder* Reactions. A Kinetic Study of the Addition of Tropone to Norbornenes

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Summary. A kinetic study of *Diels-Alder* additions between norbornene derivatives acting as dienophiles and the dienes tropone, perchlorocyclopentadiene and 9,10-dimethylanthracene is presented. The results suggest that tropone thereby acts as an electron acceptor, classifying these reactions then as *Diels-Alder* additions with 'inverse electron demand'.

The role of non-reacting double bonds was investigated using 7-alkylidenenorbornene derivatives as dienophiles. These show comparable reactivity in 'normal' but enhanced reactivity in 'inverse electron demand' *Diels-Alder* additions. This outcome is interpreted in terms of frontier orbital interactions between the reactants using photoelectron spectroscopical results as a basis for the qualitative perturbation treatment. It is suggested that the enhanced reactivity in the case of the 7-alkylidene derivatives does not necessitate the consideration of a direct ('through-space') participation of the non-reacting double bond.

Introduction. – The influence of substituent effects in *Diels-Alder* reactions has been known for a long time. For many years it was believed that apart from steric considerations high reactivity could be obtained by the presence of electron rich groups attached to the diene or of electron withdrawing groups attached to the dienophile only. To this so called *Alder* rule, however, striking exceptions have been found in recent years [1]; high rates have been observed in certain reactions between electron poor dienes and electron rich dienophiles. These were classified as 'cycloadditions with inverse electron demand' and their discovery led to the conclusion that it is the difference in electron density between the addends that is important for high reactivity.

One of the most interesting compounds in cycloaddition reactions is tropone (**10**). Along in thermally allowed reactions [2] it acts as a 2π-electron system with ketenes [3], as a 4π-system with isolated double bonds [4] and fulvenes [5], and as a 6π-system with cyclopentadiene [6]. Although the reason for this variety of reaction types is not yet known, the high stereoselectivity and regioselectivity [7] in the formation of some tropone adducts led to the assumption that secondary orbital overlap of non-reacting double bonds controls the reaction [8].

In order to get more information about cycloadditions of tropone we instigated a careful kinetic investigation. Our special interest in the influence of additional, non-reacting double bonds led us to use norbornene derivatives as dienophiles because of their availability, their simple symmetrical structures, and the rigid fixation of their double bonds. These model compounds form stable *Diels-Alder* adducts with tropone in high yields, a fact which is of importance for kinetic studies.

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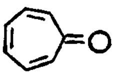
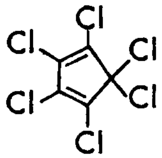
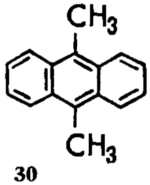
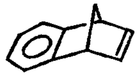
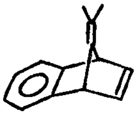
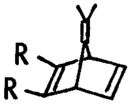
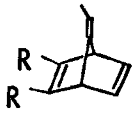
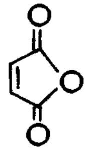
To find out whether tropone is the electron donor or acceptor in its *Diels-Alder* reactions, some further additions were investigated. The norbornene derivatives were allowed to react with hexachlorocyclopentadiene (**20**), a diene with 'low electron density', and with the electron rich 9,10-dimethylanthracene (**30**).

Results. – Reaction rates were determined by gas chromatography. Determination by UV. spectroscopy gave the same results, but with less accuracy. Use of dioxane as solvent and a large excess of dienophile together with a small amount of

Table 1. *Observed second order rate constants* k · 10^6 *of* Diels-Alder *reactions at 130° in dioxane* ($l \cdot mol^{-1} \cdot s^{-1}$)

diene dienophile		 **10**	 **20**	 **30**
	**1**	3.60	78 (72)	34 (36)
	**2**	4.54		
	**3**	3.86	*ca.* 76	65
	**4**	62.3	387	92
	**5**	1.61		41
	**6**	22.7		
	**7**	15.3		
	**8**	79.4	(29)	(1410000)

R = $COOCH_3$
( ) values by *Sauer & Wiest* [1].

hydroquinone, which was shown not to change the rates, led to clean reactions. Further details are given in the experimental part.

Table 1 shows the structures of the addends and the observed second order rate constants of *Diels-Alder* reactions at 130° in dioxane. Values in parentheses are earlier published results by *Sauer* & *Wiest* [1].

Table 2 shows the activation parameters obtained for some of the described *Diels-Alder* reactions. (As expected, large negative values were obtained for the entropy changes.)

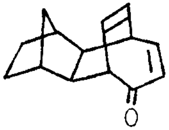
Table 2. *Activation parameter of* Diels-Alder *reactions at 100° in dioxane*

Addends	Used temp. range (°C)	$\Delta H^{\neq}$ (kcal · mol^{-1})	$\Delta S^{\neq}$ (e. u.)
Tropone **10** and norbornene **1**	135–165	20	–35
Tropone **10** and norbornadiene **2**	130–160	22	–29
Tropone **10** and benzonorbornadiene **3**	135–165	21.5	–31
Tropone **10** and isopropylidene-benzonorbornadiene **4**	120–150	20	–29
Tropone **10** and maleic anhydride **8**	120–150	19	–30
Hexachlorocyclopentadiene **20** and isopropylidene-benzonorbornadiene **4**	85–115	16	–36

The structures of the obtained adducts are also given. Of these products, **11–18**, **21**, **23**, **24**, **31**, **33**, **34**, and **35** were isolated in 71–92% yields. Except for adduct **17**, which was a 1:1 mixture of two isomers (**17a** and **17b**) resulting from the asymmetry of dienophile (**7**), all the products were easily crystallized. The NMR. spectra of the adducts **11–17** based on tropone showed two clean doublets of *AB*-type in the 2.5 ppm region (δ values) with coupling constants (due to vicinal coupling between the two endo methine H) of approximately 9 Hz. The symmetrical adducts based on hexachlorocyclopentadiene (**20**) and 9,10-dimethylanthracene (**30**) showed singlet resonances due to the endo H. Compatible with earlier findings [9] and because of the very small coupling between these hydrogens and the vicinal bridgehead H, these were classed as endo adducts, formed by the addition of dienes **10**, **20**, and **30** to the ***unsubstituted and therefore sterically unhindered double bond*** of the norbornadienes **2–7**. This is particularly striking in the addition of the electron rich 9,10-dimethylanthracene (**30**) to norbornadiene-2,3-dimethylcarboxylate (**5**), whose substituted double bond might be expected to react, because of its 'lower electron density'.

NMR. spectroscopists will be delighted with the resonances of the *syn* (with respect to the anthracene residue) methylene H of the adducts **31**, **33**, and **35**, since they are shifted by the diamagnetic anisotropy of the near benzene moiety to 0.1 ∼ –0.4 ppm, a region where usually only cyclopropyl H resonance is found.

Discussion. – *General Features.* The listed data show slightly more reactivity in the addition of tropone (**10**) to norbornadiene (**2**) than to norbornene (**1**). Since this can be attributed to a statistical factor, given that **2** contains two equivalent double



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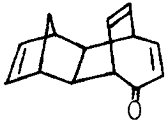

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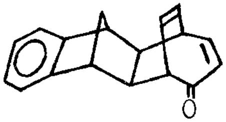

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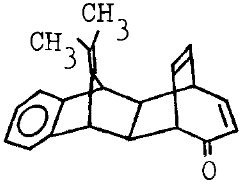

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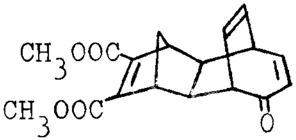

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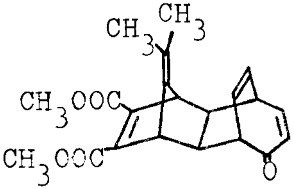

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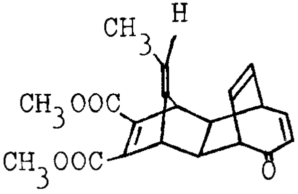

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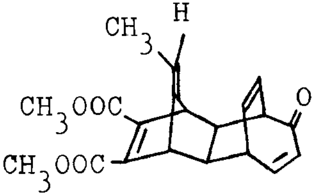

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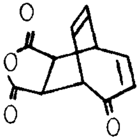

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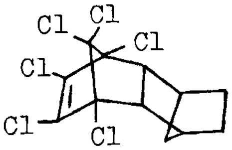

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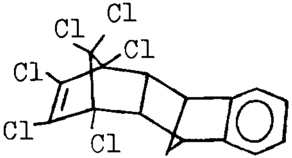

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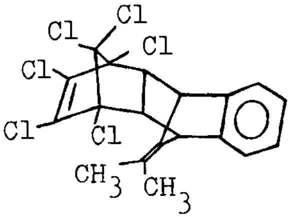

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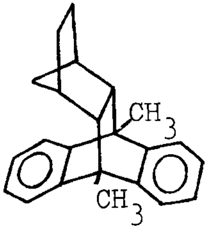

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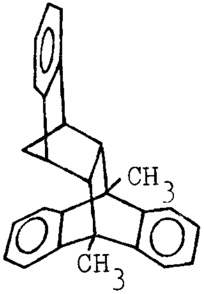

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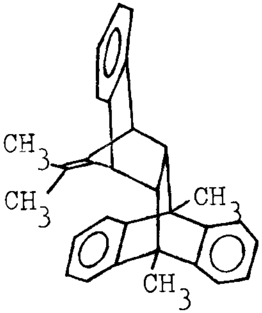

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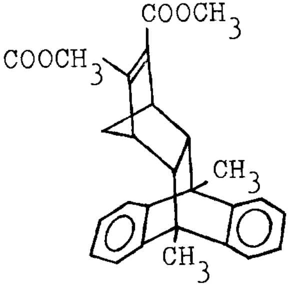

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bonds with respect to **1**, the reactivity per double bond in these two systems seems to be roughly the same. Benzonorbornadiene (**3**) showed a rate similar to **1**. A similar conclusion concerning **1** and **3** can be drawn from their reaction rates towards the more familiar dienes hexachlorocyclopentadiene (**20**) and 9,10-dimethylanthracene (**30**).

Introducing an isopropylidene group at the 7-position of benzonorbornadiene (**3**), however, led in the addition to tropone to a *sixteen fold rate enhancement.* Similar results were obtained with the dimethyl-ester derivatives **5** and **6**, the rate difference factor being 14. With the electron poor **20** a similar, but slighter effect was found too. The rate increase in the additions of the electron rich **30** however, is much less significant, probably due to more favourable steric conditions in the reaction of compound **4**. This follows in particular from the theoretical considerations outlined below, which do not point toward a rate increase with **30** from electronic factors.

Substituting one methyl group by a hydrogen in compound **6** led to a decrease in reactivity with tropone (**10**) in spite of less steric hindrance in compound **7**. This fact indicates that electronic factors are indeed significant in the above mentioned rate increase.

It is thus concluded that tropone (**10**) reacts faster with electron rich dienophiles and *therefore acts as an electron acceptor.* This is supported by its similarity to hexachlorocyclopentadiene (**20**) rather than to 9,10-dimethylanthracene (**30**) in *Diels-Alder* reactions to the norbornenes (**1**)–(**4**).

Theoretical Considerations. – The above presented experimental results shall be qualitatively rationalized in terms of perturbation theory [10]–[13], using the molecular orbital structure of the separate reactants as a basis. Following earlier experience [11a] [14] [15] only interactions between frontier orbitals and specifically, only interactions between the highest occupied MO (HOMO^{r}) of the electron rich and the lowest unoccupied MO (LUMO^{p}) of the electron poor component are considered as depicted in Fig. 1. Hence, the rate determining stabilisation of the transition state can be related to the depression $\delta\varepsilon_r$ of the HOMO^{r} by the LUMO^{p}, which is given by

$$\delta\varepsilon_r = -\frac{\mathcal{H}^2}{\Delta}. \tag{1}$$

The rate of reaction is a monotonic function of $\delta\varepsilon_r$:

$$\mathrm{rate} = \mathrm{f}\,(\delta\varepsilon_r). \tag{2}$$

In (1): $\mathcal{H} = \langle\psi_p|\mathbf{P}|\psi_r\rangle$; $\Delta = \varepsilon_p - \varepsilon_r$, $\mathcal{H}$ being the interaction element between the wave functions ψ_p and ψ_r, obtained *via* the perturbation operator **P**, and ε_p, ε_r being the corresponding orbital energies.

The following experimental observations will be discussed on this basis:

I. *Additions of 'electron poor'* **10** *to norbornadiene* (**2**) *and norbornene* (**1**) *have roughly the same rates.*

From PE. measurements [16] and assuming *Koopmans'* theorem to hold [17], it was found that – as a result of 'through space' homoconjugation [18] – the donor-MO ψ_r of **2** is shifted towards higher energies with respect to **1**, the difference ε_r (**2**) $-$ ε_r (**1**) being 0.28 eV. Hence, from equ. (1), Δ (**2**) $<$ Δ (**1**) and one might predict a larger rate of addition for **2** than for **1**. However, ψ_r (**2**) extends now over *two* double bonds, the HOMO^r electron density at the reacting centers being decreased by approximately 50% in going from **1** to **2**. This leads to $\mathcal{H}^2$ (**2**) $\approx {}^1/_2\,\mathcal{H}^2$ (**1**), *i.e.* both the numerator and the denominator in equ. (1) have decreased. In view of this, the above mentioned experimental fact, *i.e.* similar reactivity of **1** of **2**, are qualitatively understood.

II. *Enlargement of a norbornadiene system by a 7-isopropylidene group*:

a) *leads to a significant rate increase when the 'electron poor' systems* **10** *and* **20** *are used as cycloaddends* (e.g. Diels-Alder *reactions with 'inverse electron demand'*).

b) *leads to no significant rate increase for the 'electron rich' addend* **30** (*'normal'* Diels-Alder *reaction*).

The discussion of these points shall be based on the following model systems (C_{2v}-symmetry):

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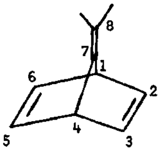

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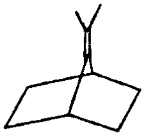

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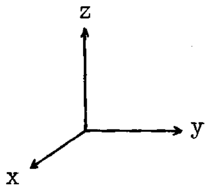

(The coordinate system as well as the orbital energies of the relevant occupied MO's are as discussed in [16]).

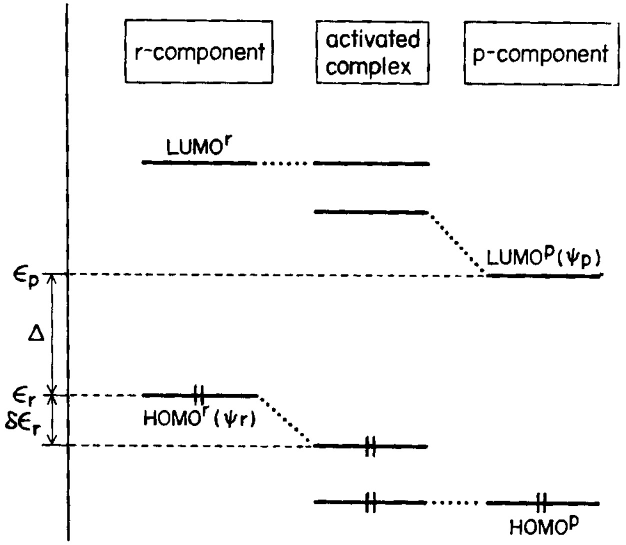

Fig. 1. *Relevant orbital interaction between HOMO^r and LUMO^p.* (Note that the HOMO^p/LUMO^r interaction is neglected)

To provide a clue for IIa, the electronic structure of **6** shall be derived on the basis of those of **2** and **9**. The orbital correlation diagram of Fig. 2 shows that the b_2-HOMO^r's of **2** and **9** are almost degenerate, thus leading after *essentially first*

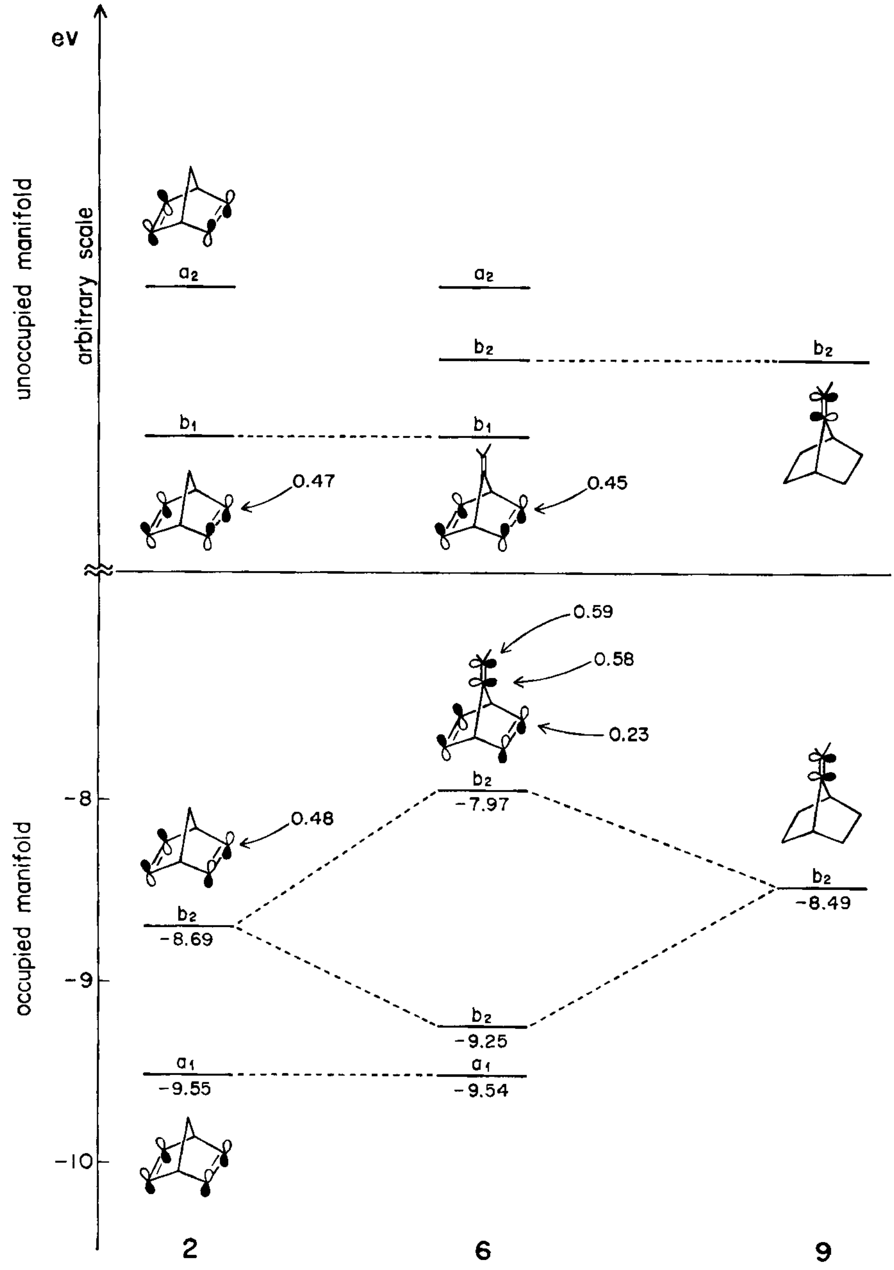

Fig. 2. *Orbital correlation diagram for the highest occupied and the lowest unoccupied π-type MO's of the model systems* **2**, **6** and **9**. Occupied orbital energies are from [16], unoccupied orbital energies are arbitrary. Values with arrows are orbital electron densities, calculated from MINDO/2-wave functions

order interaction to the $\mathbf{b}_2$-HOMO^r of **6**, the difference ε_r (**6**) $-$ ε_r (**2**) being 0.73 eV. This increase in HOMO-energy is *much larger* than the one discussed in I.

As an obvious further consequence of this interaction, the MINDO/2-HOMO^r electron density [19] at, say C_2, has decreased by about 50% in going from **2** to **6**, roughly one HOMO-electron residing now on the exocyclic isopropylidene group. This leads again to $\mathcal{H}^2$ (**6**) $\approx$ $^1/_2$ $\mathcal{H}^2$ (**2**), a relationship similar to that found in I.

Taken together: while the numerators for both I and IIa show the same 50% decrease, the denominator for IIa decreases by an amount 2.5 times larger than that in I. Thus, on the basis of no observed rate increase for I, a significant rate increase is qualitatively expected for IIa.

Note that the above arguments *do not* necessitate the consideration of a *direct* interaction of the exocyclic double bond in **6** with the incoming addend. In any case, however, such a direct participation, if present, would provide a further point for a rate increase. As shown in Fig. 3, the phases of the exocyclic basis functions in the $\mathbf{b}_2$-HOMO^r of **6** are such that any overlap with the basis functions centered at the internal C-atoms of the diene-LUMO^p would result in an *increase* of $\mathcal{H}^2$. Although this overlap would be quite small in the transition state on steric grounds, the contribution to $\mathcal{H}^2$ might still be significant, given that the HOMO^r electron density of the exocyclic double bond C-atoms (0.58, 0.59) is more than twice as large than that of the centers (0.23) which are directly attacked by the diene (see Fig. 2).

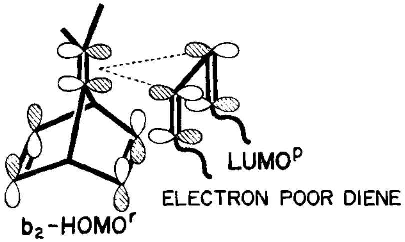

Fig. 3. *Phases of the basis functions in the* $\mathbf{b}_2$-*HOMO*^{r} *of* **6** *and in the diene-LUMO*^{p}

Fig. 2 also provides a qualitative understanding of IIb, where **3** and **4** function now as 'electron acceptors' towards **30** (Table 1). Inspection of the LUMO^p-symmetries of the model systems **2** and **9** reveals that, in contrast to the situation encountered above in the bonding MO-manifold, *no interaction* can take place in the antibonding MO-manifold. Hence, the $\mathbf{b}_1$-LUMO^p's of **2** and **6** will have roughly the

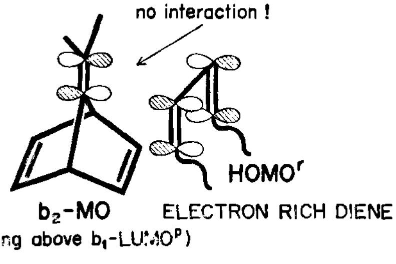

Fig. 4. *Phases of the basis functions in the unoccupied* $\mathbf{b}_2$-*MO of* **6** *and the diene-HOMO*^{r}

same orbital energy as well as the same shape. This latter point is strengthened by considering the almost identical LUMO^p-electron densities for these two systems, again obtained from MINDO/2-wave functions (*cf.* Fig. 2). As a result $\mathcal{H}^2$ as well as Δ in equ. (1) will be equal for these two compounds. Note that the electron population at the exocyclic double bond is *essentially zero* in the $\mathbf{b}_1$-LUMO^p of **6**, but large in the next highest $\mathbf{b}_2$-MO which is derived from that of **9**. However, its *symmetry forbids any interaction* with the HOMO^r of **30** as can be immediately deduced from Fig. 4.

We therefore may conclude that on a frontier orbital basis introduction of an exocyclic double bond into norbornenes does not significantly alter their reactivity in normal *Diels-Alder* additions, in agreement with the experimental findings.

Experimental Part

General. Melting points are corrected. The purity of all starting materials was confirmed by gas chromatography and NMR. spectroscopy. Concentrations in kinetic experiments are temperature corrected. They were carried out in a *Haake* R 22 thermostat with an accuracy of ± 0.1°. Kinetic gas chromatographic studies were carried out with helium as carrier gas on a *Hitachi* K 53 gas chromatograph, equipped with a temperature programmer unit and a hydrogen flame ionization detector using the following glass columns: 5% XE-60 on Chromosorb W (2 m), 1% Carbowax 20M on Chromosorb W (2 m), and 1% OV-17 on Chromosorb W (1 m). Preparative separations of adducts were carried out with helium as carrier gas on a *Yanagimoto* GCG-3 gas chromatograph using a XE-60 on Chromosorb W (2 m × 15 mm) glass column at 230°. Products of high volatility were separated by preparative thin layer chromatography on Kieselgel '*Merck*' KF_{254} using cyclohexane/isopropyl methyl ketone. – UV. spectra were taken on a *Beckmann* DK-2A, IR. spectra on a *Jasco* IR-S, NMR. spectra on a *Varian* A-60A and Mass spectra (MS) on a *Hitachi* RMU-6 spectrometer. UV. spectroscopic data are listed in nm (ε), IR. spectroscopic data in cm^{-1}, NMR. spectroscopic data as δ-values. Coupling constants J are given in Hz (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex resonance, $d \times d$ = doublet of doublets *etc.*). Assignment *endo* and *exo* was made with respect to the norbornane residue derived from the dienophile. Assignment *syn* and *anti* was made with respect to the diene **10**, **20**, and **30** residues. The value of the parent peak in mass spectra assignments is written in italics.

Kinetic Experimental. – Nine 1 ml ampoules containing 0.1 ml of a solution of 2.0 or 1.5 M of dienophile **1–8**, 0.1 M of diene **10**, **20** or **30**, 0.02 M of *n*-eicosane (internal standard) and 0.05 M hydroquinone in pure dioxane were flushed with nitrogen, sealed, and then kept in a constant temperature bath at various temperatures. At appropriate time intervals during two half-lives one ampoule was removed from the bath, cooled in ice and its contents immediately injected into a gas chromatograph. A temperature program was used for separation. From the ratios of the peak areas due to the remaining diene **10**, **20** or **30** to that of the internal standard, pseudo first order rate constants were calculated with a computer program using the least square method. These obtained rate constants divided by the molar concentration of dienophile **1–8** gave the corresponding second order rate constants. Similar rate calculations based on the increasing peak ratio of adduct to the internal standard resulted in similar but, because of the use of a peak ratio at infinite time, less accurate values. All measurements were carried out at least twice and at two different concentrations of dienophile **1–8**. The maximal calculated standard error of the reported data was ± 8%.

Preparation of Adducts. – 3 mmol dienophile **1–8**, 1 mmol of diene **10**, **20** or **30** and 0.05 mmol of hydroquinone in 1.5 ml dioxane were kept in a sealed tube under nitrogen during an appropriate time calculated from the obtained rate constants. Depending upon their molecular weights the adducts were separated by gas chromatography or by preparative thin layer chromatography, yielding 71–92% of pure material. The separated adducts were recrystallized twice from a suitable solvent.

Adduct **11** *of tropone* **10** *and norbornene* **1**. M.p. (from pentane) 72.5–73°. – UV. (ethanol): 237 (8000), 342 (115). – IR. (CCl_4): 1670 (α,β-unsat. ketone). – MS.: 200 (M^+), *131* (C_9H_7O), 28 (CO), 18 (H_2O). – NMR. (CCl_4): 0.80 (*d* × *m*, 1H, $J = 10.5$), anti methylene H; 1.0–1.7 (*m*, 4H) methylene H; 1.9–2.3 (c, 5 H) 2 *endo* methine H, 2 bridgehead H, *syn* methylene H; 3.12 and 3.38 (pair of broad *d*, 2 H, $J = 8$) bridgehead H of tropone residue; 5.51 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO; 5.8–6.4 (pair of *t*, 2 H, $J = 11$, $J = 8.5$); 6.98 (*d* × *d*, 1H, $J = 11$, $J = 8.5$) —CH =C—CO—.

$C_{14}H_{16}O$ (200.27) Calc. C 83.96 H 8.05% Found C 84.16 H 8.06%

Adduct **12** *of tropone* **10** *and norbornadiene* **2**. M.p. (from pentane) 51–52°. – UV. (cyclohexane): 222 (sh), 230 (sh), 245. – IR. (CCl_4): 1663 (α,β-unsat. ketone). – NMR. (CCl_4): 1.15 (*d* × *m*, 1H, $J = 10$) anti methylene H; 1.92–2.43 (*AB-q*, 2 H, $J = 9$) *endo* methine H; 2.43–3.42 (*m*, 5 H) bridgehead H and *syn* methylene H; 5.46 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO—; 5.46–6.60 (*m*, 4 H) vinyl H; 7.01 (*d* × *d*, 1H, $J = 11$, $J = 8$) —CH=C—CO—.

$C_{14}H_{14}O$ (198.25) Calc. C 84.81 H 7.12% Found C 84.59 H 7.10%

Adduct **13** *of tropone* **10** *and benzonorbornadiene* **3**. M.p. (from methanol) 151.5–152.5°. – UV. (ethanol): 230 (23000), 266 (2200), 1618 (1620), 344 (120). – IR. (CCl_4): 1660 (α,β-unsat. ketone). – MS.: 248 (M^+), *133* (C_9H_9O), *116* (C_9H_8), 28 (CO). – NMR. ($CDCl_3$): 1.50 (*d* × *m*, 1H, $J = 9.5$) *anti* methylene H, split into multiplet by long range coupling with *endo* methine H; 2.23 and 2.31 (*AB-q*, 2 H, $J = 9$) *endo* methine H; 2.81 (split *d*, 1H, $J = 9.5$) *syn* methylene H, split into triplet by coupling with bridgehead H; 3.0–3.7 (*c*, 4 H) bridgehead H; 5.58 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO—; 6.0–6.7 (pair of *t*, 2 H, $J = 8$) —CH=CH—; 6.9–7.3 (*c*, 6 H) aromatic H and —HC=C—CO—.

$C_{18}H_{16}O$ (248.31) Calc. C 87.06 H 6.50% Found C 87.18 H 6.46%

Adduct **14** *of tropone* **10** *and isopropylidene-benzonorbornadiene* **4**. M.p. (from methanol) 180–181.5°. – UV. (ethanol): 268 (3240), 276 (2500), 345 (126). – IR. (CCl_4): 1660 (α,β-unsat. ketone), 1375 (methyl). – MS.: 288 (M^+), 273 ($C_{20}H_{17}O$), *156* ($C_{12}H_{12}$), 141 ($C_{11}H_9$), 28 (CO), 18 (H_2O). – NMR. ($CDCl_3$): 1.52 (*s*, 3 H) methyl; 1.55 (*s*, 3 H) methyl; 1.29 and 2.34 (*AB-q*, 2 H, $J = 9$) *endo* methine H; 3.2–3.7 (*c*, 4 H) bridgehead H; 5.63 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO—; 5.8–6.5 (pair of *t*, 2 H, $J = 8$) —CH=CH—; 6.9–7.3 (*c*, 6 H) aromatic H and —HC=C—CO—.

$C_{21}H_{20}O$ (288.37) Calc. C 87.46 H 6.99% Found C 87.16 H 6.99%

Adduct **15** *of tropone* **10** *and 2,3-di(methoxycarbonyl)-norbornadiene* **5**. M.p. (from hexane/ether) 128–129°. – UV. (cyclohexane): 226 (11600), 260 (2160). – IR. (CCl_4): 1715 (ester), 1667 (α,β-unsat. ketone). – NMR. ($CDCl_3$): 1.30–1.62 (*d* × *m*, 1H, $J = 9.5$) *anti* methylene H; 2.26–2.72 (*AB-q*, 2 H, $J = 8.5$) *endo* methine H; 2.68 (*d* × *t*, 1H, $J = 9.5$, $J = 1.7$) *syn* methylene H, this signal overlaps with the signal at 2.50; 2.92–3.23 (overlapping *m*, 2H) bridgehead H in norbornene residue; 3.23–3.66 (*t* × *m*, 2 H) bridgehead H in tropone residue; 3.76 (*s*, 6 H) COOMe; 5.64 (*d* × *d*, 1H, $J = 11$, $J = 2$); 5.98–6.33 (*t* × *m*, 1H) =CH—C—CO—; 6.33–6.67 (*t* × *m*, 1H) CH=C—C—CO; 7.00–7.36 (*d* × *d*, 1H, $J = 8$) —HC=C—CO—.

$C_{18}H_{18}O_5$ (314.32) Calc. C 68.78 H 5.77% Found C 68.91 H 5.82%

Adduct **16** *of tropone* **10** *and isopropylidene-2,3-di(methoxycarbonyl)-norbornadiene* **6**. M.p. (from *n*-heptane) 121.5–122°. – UV. (cyclohexane): 235 (sh) (10600). – IR. (CCl_4): 1720 (ester), 1670 (α,β-unsat. ketone). – NMR. (CCl_4): 1.49 (*s*, 3 H) methyl; 1.53 (*s*, 3 H) methyl; 2.40 and 2.51 (*AB-q*, 2 H, $J = 9.5$) *endo* methine H; 3.0–3.5 (*c*, 4 H) bridgehead H; 3.72 (*s*, 6 H) $COOCH_3$; 5.55 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO—; 5.7–6.4 (pair of *t*, 2 H, $J = 8$) CH=CH; 7.03 (*d* × *d*, $J = 11$, $J = 8$) —CH=C—CO—.

$C_{21}H_{22}O_5$ (354.39) Calc. C 71.17 H 6.26% Found C 71.38 H 6.29%

Adducts **17a** *and* **17b** *of tropone* **10** *and ethylidene-2,3-di(methoxycarbonyl)-norbornadiene* **7** (mixture of two isomers). Oil. – UV. (ethanol): 241 (sh) (8000). – IR. (CCl_4): 1720 (ester), 1670 (α,β-unsat. ketone), 1380 (methyl). – MS.: 340 (M^+). – NMR. (CCl_4): 1.51 and 1.55 (2 *d*, 3 H, $J = 7$) CH_3C=; 2.48 (*AB-q*, 2 H, $J = 8.5$) *endo* methine H; 3.11 and 3.37 (2 *d* × *m*, 4 H, $J = 7$ and $J = 8$) bridgehead H; 3.72 (*s*, 6 H) —$COOCH_3$; 4.68 and 4.72 (2 *q*, 1H, $J = 7$) vinyl H; 5.55 (*d* × *d*, 1H, $J = 11$, $J = 2$) =CH—CO; 5.7–6.4 (*c*, 2 H) CH=CH; 7.03 (*d* × *d*, $J = 11$, $J = 8$) —CH=C—CO—. The intensities of the methyl resonances of 1.51 and 1.55 indicate a 1:1 ratio of the two isomers; the ratios between these resonances and those of the *endo* methine H exclude the presence of *exo* isomers. – NMR. (C_6D_6): 1.20 (*d*, 3 H, *J* = 7) CH_3—C=; 4.45 (*q*, 1 H, *J* = 7) Me—CH=. As these methyl resonances appear as one doublet and these vinyl resonances as one quartet in C_6D_6 but as two doublets and two quartets in CCl_4, the presence of two isomers is indicated.

Adduct **18** *of tropone* **10** *and maleic anhydride* **8**. M.p. (from acetone) 181.5–182.5°. – UV. (ethanol): 288 (7000), 342 (220). – IR. ($CHCl_3$): 1870, 1780 (anhydride), 1675 (α,β-unsat. ketone). – MS.: 204 (*M*+), *131* (C_9H_7O), 51 (C_4H_3), 28 (CO). – NMR. (d_6-DMSO): 3.5–4.2 (*c*, 4 H) *exo* methine H and bridgehead H. The signals of an *AB-q* at 3.94 (*J* = 9) overlap with complex signals; 5.74 (*d*×*d*, 1 H, *J* = 11.5, *J* = 2) =CH—CO; 6.28 and 6.67 (2 *t*, 2 H, *J* = 7) CH=CH; 7.29 (*d*×*d*, 1 H, *J* = 11.5, *J* = 9) —CH=C—CO—.

$C_{11}H_8O_4$ (204.17) Calc. C 64.74 H 3.95% Found C 65.02 H 3.99%

Adduct **21** *of hexachlorocyclopentadiene* **20** *and norbornene* **1**. M.p. (from methanol) 78.5–79°. – UV. (ethanol): 216 (5500). – IR. (CCl_4): 1600 (Cl—C=C—Cl). – MS.: 364 (*M*+), *329* ($C_{12}H_{10}Cl_5$), *66* (polyhalogenated fragments strong *P+2* and P+4 peaks). – NMR. (CCl_4): 0.8 – 1.8 (*c*, 6 H) methylene H; 2.38 (broad *s*) bridgehead H; 2.62 (*s*, 2 H) *endo* methine H.

$C_{12}H_{10}Cl_6$ (366.94) Calc. C 39.28 H 2.75 Cl 57.98% Found C 39.21 H 2.78 Cl 57.70%

Adduct **23** *of hexachlorocyclopentadiene* **20** *and benzonorbornadiene* **3**. M.p. (from methanol) 133–134°. – UV. (ethanol): 259 (660), 265 (980), 272 (1040). – IR. (CCl_4): 1600 (Cl—C=C—Cl). – MS.: 413 (*M*+), 378 ($C_{16}H_{10}Cl_5$), *129* (polyhalogenated fragments strong *P+2* and P+4 peaks). – NMR. (CCl_4): 1.56 (*d*×*m*, 1 H, *J* = 11) *anti* methylene H, long range coupling with *endo* methine H; 1.91 (*d*×*t*, 1 H, *J* = 11) *syn* methylene H, split into triplet by coupling with bridgehead H (*J* = 1.5); 2.73 (*s*, 2 H) *endo* methine H; 3.36 (broad *s*, 2 H) bridgehead H; 7.1 (broad *s*, 4 H) aromatic H.

$C_{16}H_{10}Cl_6$ (414.98) Calc. C 46.31 H 2.43 Cl 51.27% Found C 46.46 H 2.34 Cl 51.08%

Adduct **24** *of hexachlorocyclopentadiene* **20** *and isopropylidene-benzonorbornadiene* **4**. M.p. (from methanol) 150.5–151°. – UV. (ethanol): 263 (2150), 269 (2630), 276 (2450). – IR. (CCl_4): 1600 (Cl—C=C—Cl), 1375 (methyl). – MS.: 453 (*M*+), 418 ($C_{19}H_{14}Cl_5$), *186* (polyhalogenated fragments strong *P+2* and P+4 peaks). – NMR. (CCl_4): 1.66 (*s*, 6 H) methyl; 2.81 (*s*, 2 H) *endo* methine H; 3.80 (*s*, 2 H) bridgehead H; 7.1 (broad *s*, 4 H) aromatic H.

$C_{19}H_{14}Cl_6$ (455.04) Calc. C 50.15 H 3.10 Cl 46.75% Found C 50.36 H 3.22 Cl 46.55%

Adduct **31** *of 9,10-dimethylanthracene* **30** *and norbornene* **1**. M.p. (from ethanol) 154.5–155°. – UV. (ethanol): 266 (1210), 274 (1460). – IR. (CCl_4): 1455, 1375 (methyl). – MS.: 300 (*M*+), *206* ($C_{16}H_{14}$), 204 ($C_{16}H_{12}$). – NMR. ($CDCl_3$): – 0.40 (*d*×*m*, 1 H, *J* = 11) *syn* methylene H; 0.30 (*d*×*m*, 1 H, *J* = 11) *anti* methylene H. This signal is more complex than that of the *syn* methylene H, because of long range coupling with the *endo* methine H; 0.8–1.5 (*c*, 4 H) methylene H; 1.67 (*d*, 2 H, *J* = 1) *endo* methine H; 1.93 (*s*, 6 H) methyl; 2.06 (*m*, 2 H) bridgehead H; 7.16 (*m*, 8 H) aromatic H.

$C_{23}H_{24}$ (300.42) Calc. C 91.95 H 8.05% Found C 92.24 H 8.09%

Adduct **33** *of 9,10-dimethylanthracene* **30** *and benzonorbornadiene* **3**. M.p. (from 2-propanol) 170–170.5°. – UV. (ethanol): 261 (1360), 267 (2200), 274 (2600). – IR. (CCl_4): 1450, 1375 (methyl). – MS.: 348 (*M*+), *206* ($C_{16}H_{14}$). – NMR. ($CDCl_3$): 0.12 (*d*×*t*, 1 H, *J* = 10, *J* = 1.5) *syn* methylene H; 1.00 (*d*×*m*, 1 H, *J* = 10) *anti* methylene H. This signal is more complex than that of the *syn* methylene H, because of long range coupling with the *endo* methine H; 1.85 (*d*, 1 H, *J* = 1) *endo* methine H; 2.03 (*s*, 6 H) methyl; 3.09 (*t*, 1 H, *J* = 1); 6.8–7.4 (*c*, 12 H) aromatic H.

$C_{27}H_{24}$ (348.46) Calc. C 93.06 H 6.94% Found C 92.97 H 6.94%

Adduct **34** *of 9,10-dimethylanthracene* **30** *and isopropylidene-benzonorbornadiene* **4**. M.p. (from 2-propanol) 202.5–203°. – UV. (ethanol): 265 (2400), 270 (3150), 277 (3200). – IR. (CCl_4): 1450, 1375 (methyl). – MS.: 388 (*M*+), *372* ($C_{29}H_{25}$), 206 ($C_{16}H_{14}$). – NMR. ($CDCl_3$): 1.10 (*s*, 6 H) $[CH_3]_2C$=; 1.89 (*s*, 2 H) *endo* methylene H; 2.01 (*s*, 6 H) methyl; 3.53 (*s*, 2 H) bridgehead H; 6.8–7.4 (*c*, 12 H) aromatic H.

$C_{30}H_{28}$ (388.52) Calc. C 92.74 H 7.26% Found C 92.83 H 7.35%

Adduct **35** *of 9,10-dimethylanthracene* **30** *and 2,3-di(methoxycarbonyl)-norbornadiene* **5**. M.p. (from methanol) 153.5–154.5°. – UV. (ethanol): 266 (3600) sh, 274 (1960). – IR. (CCl_4): 1720 (ester), 1380 (methyl). – MS.: 414 (M^+), 383 ($C_{26}H_{23}O_3$), *206* ($C_{16}H_{14}$). – NMR. ($CDCl_3$): –0.09 ($d \times t$, 1 H, $J = 10.5$, $J = 1.5$) *syn* methylene H; 1.90 ($d \times m$, 1 H, $J = 10.5$) *anti* methylene H. This signal is more complex than that of the *syn* methylene H, because of long range coupling with the *endo* methine H; 1.97 (*s*, 6 H) methyl; 2.10 (*d*, 2 H, ($J = 1$)) *endo* methine H; 2.97 (*t*, 1 H, $J = 1$) bridgehead H; 3.69 (*s*, 6 H) —$COOCH_3$; 7.20 (*m*, 8 H) aromatic H.

$C_{27}H_{26}O_4$ (414.48) Calc. C 78.24 H 6.32% Found C 78.31 H 6.42%

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