240. The Effects of Homoconjugated Cyclopropane and Oxirane Rings on the *Diels-Alder* Reactivity of 2,3-bis(methylidene)norbornane[1])[2])

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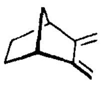
Dedicated to Professor Dr. *Edgardo Giovannini* on his 70th anniversary

(24.VII.79)

Summary

Preparation of 6*exo*,7*exo*-bis(methylidene)-tricyclo$[3.2.1.0^{2,4}]$octane (**6**) is described. The reactivity of **6** towards tetracyanoethylene is evaluated and compared with that of *exo*-2,3-epoxy-5,6-bis(methylidene)norbornane (**5**), 2,3-bis(methylidene)norbornane (**1**) and other related dienes. The cyclopropane group in **6** exerts an unsignificant rate retardation effect on the *Diels-Alder* reactivity of this diene relative to that of **1**, whereas a relatively important rate retardation effect is caused by the *exo*-oxirane ring in **5**. The observed effects are probably due to electronic factors (through-space and through-bond interactions).

Introduction. - Chemical and spectroscopic properties of the s-*cis*-butadiene function in 2,3-bis(methylidene)norbornane (**1**) can be modified without direct substitution of the diene moiety [1-8]. We have found that the hydroxyl substituents in the alcohol **2** and diol **3** have an insignificant rate retardation effect on the *Diels-Alder* reactivity of these dienes towards dimethyl acetylenedicarboxylate (DMA) and a very small rate retardation effect on that towards tetracyanoethylene (TCE) [2]. The carbonyl group in 5,6-bis(methylidene)-2-norbornanone (**4**) caused, however, a significant rate retardation effect, although not as large as that observed for *exo*-2,3-epoxy-5,6-bis(methylidene)-norbornane (**5**), relative to the parent diene



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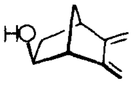

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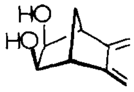

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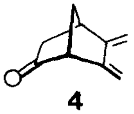

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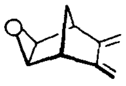

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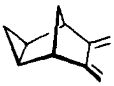

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[1]) 'Interaction between non-conjugated chromophores', part 9; part 8 [1], part 7 [2], part 6 [3], part 5 [4], part 4 [5], part 3 [6], part 2 [7], part 1 [8].

[2]) This work has been presented to the fall meeting of the 'Société suisse de chimie', Bern, oct. 1978.

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1. These observations suggested that the effect caused by the epoxide ring in **5** on the chemical and spectroscopic properties of this exocyclic diene [9] were probably the manifestations of strain introduced into the bicyclic skeleton and/or specific electronic features (*i.e.*, low-lying empty orbitals, electrophilicity) of the oxirane ring [2]. To a first approximation, the strain introduced by the epoxy substituent in **5** must be the same as that introduced by the cyclopropane ring [10] in the *exo*-6,7-bis(methylidene)-tricyclo[3.2.1.$0^{2,4}$]-octane (**6**). Thus, the comparison of the properties of the dienes **5** and **6** relative to those of **1** should help us in determining whether the strain factor or the electronic factor is the dominant one when making the epoxy-diene **5** a poorer diene than **1** towards strong dienophiles. The geometry of the diene (distance between the methylidene carbon atoms [11], deviations from planarity [12]) should be very similar for **1**-**6**, as resulting also from MINDO/3 calculations [13].

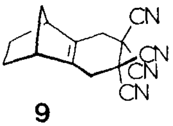
We have now prepared the tricyclic diene **6** and we shall compare its reactivity towards TCE with that of other 2,3-bis(methylidene)norbornanes.

Results and discussion. - The *trans*-5,6-bis(chloromethyl)-2-norbornene (**7**) is readily available by *Diels-Alder* addition of cyclopentadiene to *trans*-1,4-dichloro-2-butene [14]. The olefin **7** reacted with diazomethane in the presence of 1% of $Pd(OAc)_2$ [15] (ether, 20°, 12 h) yielding the cyclopropane derivative **8** (88%). When heated in boiling ethanol (65 h) with a large excess of KOH, **8** eliminated two mol-equivalents of HCl to give the tricyclic diene **6** (70%).

7 **8**

Cyclopropanations of norbornene derivatives [16] have been found to be stereoselective and to yield *exo*-tricyclo-[3.2.1.$0^{2,4}$]octanes. The *exo*-configuration of **6** is confirmed by the absence of a $^3J(H,H)$ coupling between the bridgehead hydrogen atoms H–C(1,5) and H(*endo*-C(2),C(4)) [2] [17]. The ^{13}C-NMR. spectrum of **6** compared with that of **1** showed a γ-effect of -13.0 ppm on the δ_c of C(7) for the *exo*-2,3-methylene substituent of norbornane. Similar upfield γ-effects have been reported for the δ_c of C(7) in *exo*-2,3-methylene-norbornane [18], -norborn-5-ene and -benzonorborn-5-ene derivatives [19] (a positive γ-effect of *ca.* 15 ppm on δ_c of C(7) is expected for the *endo*-2,3-methylene substituent [18] [19]). The UV. absorption spectrum of **6** showed a $\lambda_{max} = 243$ nm (isooctane or ethanol) for its $V \leftarrow N$ transition; this lies between the λ_{max} measured for **1** (248 nm [2] [9] [20]) and **5** (239 nm [7] [9]).

The *Table* summarizes our kinetic data on the *Diels-Alder* cycloadditions of the dienes **1**, **5** and **6** to TCE in toluene. The expected adducts **9** [21], **10** and,



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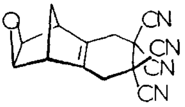

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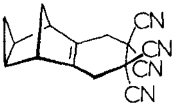

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Table. *Kinetic data of cycloadditions of dienes* **1**, **5**, **6** *to TCE in toluene*

Diene	k^{II} [10^4 l mol^{-1}s^{-1}] Statistical standard deviation[a]) Temperature of the measurements above (K)					$\Delta H^{\neq}$ [kcal mol^{-1}]	$\Delta S^{\neq}$ cal mol^{-1}K^{-1}
1	125	269	512	979	1870	10.9	−27.3
	±1	±1	±4	±20	±10	±0.6	±2.2
	272.7	283.9	293.4	302.5	313.0	T_m:	293
5	2.87	6.61	14.1	29.2	56	13.4	−28.8
	±0.2	±0.2	±0.2	±0.5	±1	±0.2	±0.7
	292.4	302.6	312.9	323.3	332.2	T_m:	312
6	55.6	109	213	416	753	11.6	−27.8
	±1	±2	±2	±6	±10	±0.2	±0.8
	283.9	293.3	302.6	312.9	323.0	T_m:	303

[a]) For 6 to 10 independent measurements with 3 different solutions of the dienes and TCE.

respectively, **11** were the only products formed and could be isolated (see experimental part). The reactions were followed for 3 half-lives and were found to obey pseudo-first order rate laws (k'^{I}) for the disappearance of the TCE-toluene complex (λ_{max} = 405 nm) when a 30- to 1000-fold excess of the dienes **1**, **5** or **6** was used. There was no observable effect on the second order rate constant k^{II} due to changes of the initial concentration of the cycloaddends ([TCE] = (1.5-4.6) · 10^{-4}M; [diene] = 5.8 · 10^{-3}-1.9 · 10^{-1}M) and due to changes in their initial concentration ratios.

An *Arrhenius* plot of the measured values of $k^{II} = k'^{I}$/[diene] *vs.* 1/T allowed the evaluation of the activation parameters. For all the reactions investigated, the $\Delta S^{\neq}$ terms are found to have comparable values; therefore, the enthalpy terms $\Delta H^{\neq}$ are responsible for differentiating the reactivity of the dienes **1**, **5** and **6** towards TCE/toluene.

The comparison of the rate constants of the cycloadditions of TCE to 2,3-bis-(methylidene)norbornane (**1**) and *exo*-5,6-bis(methylidene)-2,3-epoxynorbornane (**5**) shows a retardation effect of 1/178 at 20° due to the introduction of the *exo*-oxirane ring in **5**. A similar effect was observed on comparing *Diels-Alder* additions of DMA to **1** and **5** and to the corresponding 7-oxa-norbornane analogues [5]. A much smaller retardation effect of 1/5 (at 20°) is found on comparing the rate constants of the cycloadditions of **1** and of the tricyclic diene **6** to TCE.

The reactivity differences observed here are not very large on an absolute scale; nevertheless we think that they are significant when considering the fact that all our dienes are grafted on very similar, rigid norbornane skeletons and that we are dealing with remote substituent effects. Our results must be compared with the *Diels-Alder* additions of the compounds listed here-below where the different substituents are attached directly to the diene function [22] [23][5]).

An exothermicity of 30-40 kcal/mol is estimated for the additions of TCE to **1**-**6** [26]. This corresponds to about three times the measured $\Delta H^{\neq}$. Assuming a

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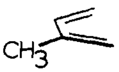
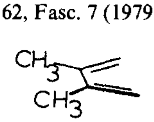
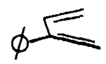
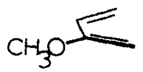
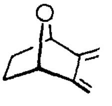
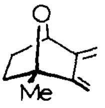
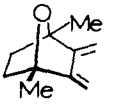
[5]) See also the cycloadditions of tropone to norbornene, cyclopentadiene and anthracene derivatives [24] and other *Diels-Alder* reactions [25].

						
maleic anh./ benzene, 25°:	$k_{\text{rel}}^{\text{II}}$:	(1.0)	~3	~11		~10 [22]
TCE/CH$_2$Cl$_2$, 20°:	$k_{\text{rel}}^{\text{II}}$:		(1.0)		~4.4	~40 [23]

one-step mechanism [27] and validity of the *Bell-Evans-Polanyi* principle [28], the properties of the starting dienes and dienophiles might affect the activation energies of the cycloadditions of **1**-**6** to TCE and other dienophiles. Steric hindrance between the cycloaddends were not expected [5] to perturb significantly the additions of **1**-**6** to TCE and DMA. This was confirmed on comparison of the rate constants of the *Diels-Alder* additions of the 2,3-bis(methylidene)-7-oxa-norbornanes [5]:

				
$k_{\text{rel}}^{\text{II}}$:	(1.0)	~1.	~1.	(DMA/CCl$_4$, 25°) [5]
$k_{\text{rel}}^{\text{II}}$:	(1.0)	~1.4	~2.	(TCE/CH$_2$Cl$_2$, 25°)[6]

To a first approximation, and assuming group additivity rules [29] to be valid in our cases, the strain energy introduced into the bicyclic skeleton is expected to be the same for cyclopropanation and epoxidation of the norbornane system [10]. The fact that the cyclopropane-diene **6** reacts with TCE 35 times faster at 20° ($\Delta\Delta H^{\neq} \simeq 2$ kcal/mol for $\Delta H^{\neq} \simeq 11$ kcal/mol) than the epoxy-diene **5** and only 5 times more slowly than the parent diene **1** strongly suggest that strain effects are not the most important factors that modify the *Diels-Alder* reactivity of **1**-**6**. Our kinetic results support the hypothesis that electronic factors play a non-negligeable role in decreasing the reactivity of the epoxy-diene **5** relative to **1**.

Long-range interactions of cyclopropyl groups with carbenium ion centres [30] and unsaturated functions [31] are well documented. Little is known however about homoconjugative interactions involving oxiranes. Epoxide participation was found to be absent in the ionization of isomeric 6-oxabicyclo-[3.1.0]hexan-3-yl tosylates [32]. The weak resonance donating effect of the three-membered ring [33] being overwhelmed by the inductive withdrawing ability of the epoxide. The electronegativity of the oxygen atom alone cannot explain the rate ratio of the cycloadditions of **5** and **1**, since we have found the hydroxy derivatives **2** and **3** to react faster than **5** towards TCE and DMA [2]. Thus, the specific electronic characteristics of the oxirane substituent must be involved. Molecular orbital (MO) calculations [34] show that ethylene oxide has a lower lying LUMO than cyclopropane and furthermore this orbital has relatively large coefficients at the carbon atoms[7] that are well oriented for a homoconjugative stabilization of the HOMO of the diene (see below).

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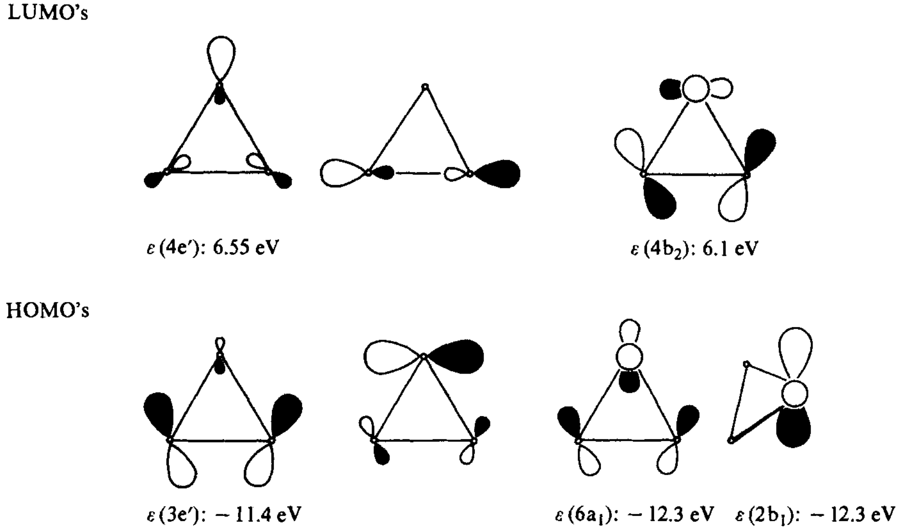
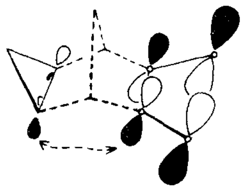
[6] By a competitive GC. technique, see [2].

[7] This is confirmed experimentally by a *Hammett* ρ value larger for *m*- and *p*-substituted 2,3-epoxy-3-phenylpropionic acids than for the corresponding 2-phenylcyclopropanecarboxylic acids [35]. The electrophilic character of the epoxide substituent compared with the cyclopropyl substituent has also been shown by S_N1 solvolysis data [36] and by photoelectron spectroscopic data [37].



The HOMO (diene)-HOMO (cyclopropane) interaction in **6** is expected to be of small importance because of the unfavourable shape of the HOMO (3e', e_A becoming a'' in **6**) for an overlap with the HOMO localized on the diene in **6**. This hypothesis is confirmed by photoelectron spectroscopy of 6,7-bis(methylidene)-tricyclo[3.2.2.$0^{2,4}$]nonane and 2,3-bis(methylidene)bicyclo[2.2.2]octane derivatives [31b]. An even smaller effect is expected for the 'through-space' and 'through-bond' HOMO (diene)-HOMO (oxirane) interaction in **5** because the σ_{CO} (3b_2, becoming a'' in **5**) MO of the ethylene oxide (see [34]) is relatively low-lying and concentrates its electron density at the oxygen atom. Therefore according to these very qualitative predictions, the HOMO of the epoxy-diene **5** must be lower-lying than those of **1**, **2**, **3** and **6** because of the long-range oxirane-diene interactions8) (that constitutes a



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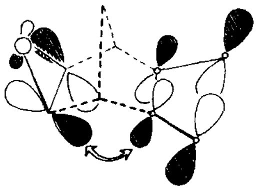

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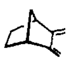
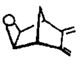
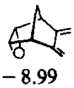
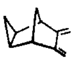
8) MINDO/3 calculations [39] (with complete geometry minimization) gave the following frontier MO's [13] in agreement with our qualitative interpretation.

						
HOMO:	− 8.97	− 8.99	− 9.16	− 8.99	− 8.93	− 8.94 eV
LUMO:	1.10	1.04	0.90	1.09	1.12	1.11 eV

The differences calculated between the *exo*- and *endo*-5,6-bis(methylidene)-2,3-epoxynorbornanes confirms the importance of the LUMO(epoxide)-HOMO(diene) stabilizing interaction. However, caution must be exerted when applying our findings to other systems since the effects discussed here are not very large.

deviation from group additivity rule for ring strain, stabilizing **5** with respect to **6**) and might be responsible, at least in part, for the lower *Diels-Alder* reactivity of **5** compared with that of **1**, **2**, **3** and **6**. The epoxide ring in **5** could also destabilize the transition states of the cycloadditions by perturbing their polarized configurations (*e.g.* charge-transfer configurations [38]; deviation from the *Bell-Evans-Polanyi* principle).

The difference in reactivity between the dienes **5** and **6** is not limited to the *Diels-Alder* addition of TCE only. We have found that the addition of bromine in CCl$_4$ and in the dark was about 5 times more rapid at 25° for the tricyclic diene **6** than for the epoxy-diene **5**[9]). Mono-epoxidation with *m*-chloroperbenzoic acid in CCl$_4$ was also observed to be about 4 times faster (25°) for **6** than for **5**[9]). These two latter reactions, as for the cycloadditions with strong dienophiles, 'calibrate' the electron donating ability of the dienes **5** and **6**. The higher reactivity of **6** compared with **5** towards electrophilic reagents confirms our qualitative interpretation for the transannular interaction between an exocyclic diene grafted on the norbornane skeleton and an homoconjugated *exo*-cyclopropane or *exo*-oxirane group.

Finally, we found that HCl-eliminations by *t*-BuOK/THF[10]) went 10-15 times faster at 40° for **12** than for **8**, thus confirming the enhanced long range electrophilic ability of the epoxide function with respect to the cyclopropane group.

8 **12**

We are grateful to the *Swiss National Science Foundation* (FN 2.891-0.77), to *Fonds Herbette*, Lausanne and to *Stipendienfonds der Basler Chemischen Industrie* for generous support.

Experimental Part

General Remarks. Melting points (m.p.) and boiling points (b.p.) (not corrected), *Tottoli* apparatus; IR. spectra ($\tilde{\nu}$[cm^{-1}]), *Beckman* IR-20A spectrometer; UV. spectra, *Carl Zeiss* RPQ 20A/C and *Pye Unicam* SP 8-100 instruments (λ_{max}[nm] (ε)); Mass spectra (MS. (EI)) at 70 eV, CEC 21-490 *Bell-Howell* spectrometer (m/z[amu] (% base peak)); ^{1}H-NMR. spectra, *Bruker* WP 80 CW spectrometer (δ[ppm] (multiplicity, apparent coupling constant J[Hz], number of protons); s = singlet, br. = broad, d = doublet, t = triplet, qa = quartet, m = multiplet, δ_{TMS} = 0.0 ppm. ^{13}C-NMR. spectra, *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT mode).

Analytical gas chromatography (GC.), *Hewlett Packard* HP 5710A chromatograph. Elementary analysis, by the 'microlabor' of the University of Geneva (Dr. *K. Eder*). Abbreviations: i.V. = *in vacuo*, RT. = room temperature, anh. = anhydrous, sh. = shoulder.

6exo,7exo-*Bis(chloromethyl)-tricyclo[3.2.1.0^{2,4}]octane* (**8**). A solution of diazomethane (prepared from 14 g of *N*-methyl-*N*-nitroso-urea [40]) in ether (200 ml) was added portionwise to a solution of *trans*-5,6-bis(chloromethyl)norborn-2-ene [14] (9.6 g, 0.05 mol) in 50 ml of ether containing 0.10 g of

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[9]) By a competitive GC. technique.

[10]) No trace of the mono-olefins could be detected during the HCl-eliminations from **8** and **10**, thus confirming that elimination of the first equivalent of HCl is the rate determining step. We wish to thank Mr. *C. Pattaroni* and Mr. *E. Sutcliffe* for their participation in these measurements.

$Pd(OAc)_2$ cooled to 0°[11]). The mixture was stirred for 12 h at 20°. After filtration, the solution was concentrated and **8** was distilled i.V. 91 g (88%), colourless liquid, b.p.: 100°/1 Torr. - UV. (iso-octane): end absorption. - IR. (film): 3080, 3020, 2980, 2960, 1500, 1460, 1330, 1300, 1290, 1045, 815, 740, 715. - ^{1}H-NMR. (CCl_4): 3.8-3.3 (*m*, 4 H); 2.5 (*m*, 1 H); 2.3 (*m*, 1 H); 2.1-0.4 (*m*, 7 H); 0.3-0.0 (*m*, 1 H). - MS.: 208(0.3), 206(1.5), 204(2.3), 171(3), 169(8), 162(11), 155(23), 127(14), 119(16), 91(28), 80(37), 79(100), 78(21), 77(11).

$C_{10}H_{14}Cl_2$ (205.13) Calc. C 58.55 H 6.88% Found C 58.63 H 7.05%

*6*exo,*7*exo-*Bis(methylidene)-tricyclo[3.2.1.0^{2,4}]octane* (**6**). A mixture of **8** (3.5 g, 0.017 mol), KOH (4.0 g, 0.071 mol) and 10 ml anh. ethanol was heated under reflux for 67 h. After cooling to RT. 40 ml of H_2O were added and the mixture was extracted with pentane (3× 10 ml). The extract was dried ($MgSO_4$) and concentrated. The residue was distilled i.V.: 1.58 g (70%), colourless oil, b.p.: 45°/2 Torr. - UV. (iso-octane): 251 (sh., 5930), 243(9310), 236.5(8650). - UV. (96% ethanol): 251 (sh., 5180), 243(7930), 237(7650). - UV. (gaz): 245.5(sh.), 238, 232(sh). - IR. (CH_2Cl_2): 3000, 1670, 1650, 1500, 1450, 1310, 1095, 1030, 990, 900, 830. - ^{1}H-NMR. (CCl_4): 5.03 (br. *s*, 2 H); 4.74 (br. *s*, 2 H); 2.74 (br. *s*, 2 H); 1.28-0.50 (*m*, 5 H); 0.2 (*m*, 1 H, $J=6$). - ^{13}C-NMR. ($CDCl_3$: CCl_4 1:1): 152.4 (*s*, C(6,7)); 100.0 (*t*, ${}^1J_{CH}=156$, C(6',7')); 44.2 (*d*, ${}^1J_{CH}=147$, C(1,5)); 26.3 (*t*, ${}^1J_{CH}=136$, C(8)); 15.0 (*d*, ${}^1J_{CH}=174$, C(2,4)); 4.2 (*d*×*d*, ${}^1J_{CH}=162$, 157, C(3)). - MS.: 132(61), 131(32), 117(100), 115(29), 104(28), 91(78), 79(41), 78(34), 77(22).

$C_{10}H_{12}$ (132.21) Calc. C 90.85 H 9.15% Found C 91.10 H 9.12%

Adduct of **6** *with TCE.* The diene **6** (66 mg, 0.5 mmol) was added to a solution of TCE (70 mg, 0.55 mmol) in anh. benzene (3 ml) and stirred at RT. for 24 h. After evaporation of the solvent, the crude adduct was recrystallized in ether; yield: 98 mg (75%), white crystals, m.p.: 222-223°. - UV. (96% ethanol): 212.5(9730). - IR. (KBr): 3090, 3010, 2980, 2940, 2250, 1480, 1440, 1430, 1295, 1240, 1210, 1130, 1090, 1055, 1005, 960, 940, 820, 730. - ^{1}H-NMR. (CD_3COCD_3): 3.67 (br. *s*, 4 H); 2.95 (br. *s*, 2 H); 1.72-0.74 (*m*, 6 H). - MS.: 261(18), 260(92), 132(100), 117(94), 104(72), 91(42).

$C_{16}H_{12}N_4$ (260.30) Calc. C 73.83 H 4.65% Found C 73.96 H 4.54%

Adduct of **6** *with 4-phenyl-4*H*-1,2,4-triazolin-3,5-dione.* The diene **6** (66 mg, 0.5 mmol) was added to a solution of freshly sublimed 4-phenyl-4*H*-1,2,4-triazolin-3,5-dione *(Fluka)* (88 mg, 0.5 mmol) in CH_2Cl_2 (3 ml). Decoloration occurred in a few seconds. After evaporation of the solvent i.V., the residue was recrystallized in hexane: 120 mg (78%), m.p.: 167-170°, white crystals. - IR. (KBr): 3090, 3000, 2980, 2960, 1790, 1710, 1615, 1515, 1460, 1430, 1370, 1315, 1290, 1250, 1140, 770, 725, 720, 695, 650. - ^{1}H-NMR. ($CDCl_3$): 7.68 (*m*, 5 H); 4.47 (A_2B_2, 2 H, J(AB)= 13.); 4.43 (A_2B_2, 2 H, J(AB)= 13.); 2.92 (br. *s*, 2 H); 1.68-0.75 (*m*, 6 H). - MS.: 308(20), 307(100).

$C_{18}H_{17}O_2N_3$ (307.35) Calc. C 70.34 H 5.58% Found C 70.38 H 5.66%

Adduct of **5** *with TCE.* The 5*exo*,6*exo*-bis(methylidene)-2,3-epoxynorbornane **5** [42] (72 mg, 0.54 mmol) was added to a solution of TCE (66 mg, 0.51 mmol) in anh. benzene (3 ml) and stirred at RT. for 26 h. The white precipitate was filtered off and washed with ether: 59 mg (44%), m.p.: 185-186° (dec.), white powder. - UV. (96% ethanol): 216(9600). - IR. (KBr): 3000, 2970, 2880, 2255, 1440, 1375, 1285, 1240, 1230, 1195, 1100, 1005, 980, 910, 855, 805. - ^{1}H-NMR. (CD_3COCD_3): 3.73 (br. *s*, 4 H); 3.68 (br. *s*, 2 H); 3.15 (br. *s*, 2 H); 1.74 (*d*×*m*, 1 H, $J=10$); 1.44 (*d*×*m*, 1 H, $J=10$). - MS.: 263(18), 262(91), 233(23), 206(87), 179(45), 134(100), 105(43), 104(33), 91(43).

$C_{15}H_{10}N_4O$ (262.27) Calc. C 68.69 H 3.84% Found C 68.86 H 3.96%

Kinetic measurements. The reactions of dienes **1**, **5** and **6** (purified by distillation, 100% by GC., TLC.) with TCE (*Fluka*, recrystallized twice in chlorobenzene and sublimed (80-90°, 0.1 Torr just before use) were followed by visible absorption spectroscopy; *Pye Unicam* SP 8-100. The disappearance of the TCE/toluene (solvent) charge-transfer complex at 405 nm was measured as a function of time

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[11]) Anh. CuCl with traces of $Pd(OAc)_2$ is a very good catalyst for that reaction [41].

(automatic recording of data on floppy disc, 4 cells simultaneously with automatic cell interchange). Least square regressions were made directly on the exponential laws (computer). The pseudo-first order rate constants were found from 6-10 independent measurements at the same temperature (varying the concentrations of TCE and of the dienes). In a typical run, 2 ml of a toluene solution of the diene were placed in a cell (0.1, 0.5 or 1 cm, quartz) and allowed to equilibrate in the spectrophotometer for 20 min. Then, 5 to 10 µl of a solution of TCE in toluene were added *via* a syringe and absorbance measurements started 5 min. later. Corrections of the volume were made for thermal dilatation.

The cells were weighed before and after the kinetic: control for 'accidental' evaporation. Toluene (*Fluka, puriss. p.a.*) was purified before use by passing it through a column of neutral Al_2O_3 and SiO_2. Degassing, by bubbling dry Ar. Thermostatization, Thermostat *Haake* (±0.02°) with high flow pump. Temperature reading, directly in the cells by a Pt resistance (Pt-100) that was gauged against a quartz thermometer (*Hewlett-Packard*, 2804A). Temperature stabilization inside the cells: better than ±0.05°.

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