On the Mechanism of Diels-Alder Reactions of Nitroso Alkenes: *exo/endo* Selectivity, Stereospecificity, *E/Z* Selectivity, and Relative Reactivity of Various Olefins[1)]

Hans-Ulrich Reißig*, Claudia Hippeli[2)], and Thomas Arnold

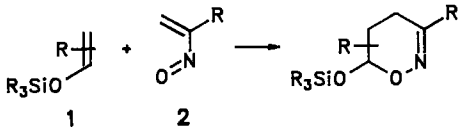
Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 22, D-6100 Darmstadt

Received May 23, 1990

Key Words: 1,2-Oxazines / Hetero Diels-Alder reactions / Nitroso alkene cycloaddition / *exo:endo* Selectivity / Stereospecificity / Silyl enol ethers, relative reactivity of

The mechanism of the hetero Diels-Alder reaction of nitroso alkenes **2** with silyl enol ethers and other olefins has been investigated. Using the bicyclic nitroso compound **2a** a study of the *exo/endo* selectivity has demonstrated that the *exo* approach is preferred with the siloxyethene **1a** as dienophile. On the other hand, the siloxycyclopentene **1c** gives a mixture of cycloadducts **3c** with an excess of *endo* product (*endo:exo* = 82:18). The stereospecificity of the nitroso alkene cycloaddition could be demonstrated with the stereochemically homogeneous silyl enol ethers **1b** and **1d**. Experiments with enol ethers **1f** and **1g** also occur stereospecifically. α-Nitrososytyrene **2b** reveals surprisingly high $k_{E/Z}$ values when *E/Z*-isomeric olefins are compared in competition experiments. Also, a detailed reactivity scale of **2b** including various structurally different silyl enol ethers and other typical dienophiles shows that a complex interplay of electronic and steric effects is operating. The large influence of steric effects is taken as evidence for a highly ordered transition state in the cycloaddition. All mechanistic details for the Diels-Alder reactions of nitroso alkenes **2** with (silyl) enol ethers are in strong accord with a concerted mechanism and exclude the involvement of zwitterions or diradicals as intermediates.

In a previous account[3)] we have reported on the regioselective synthesis of 6-siloxy-substituted 5,6-dihydro-4*H*-1,2-oxazines (abbreviated as 1,2-oxazines) from silyl enol ethers **1** and nitroso alkenes **2**. According to Gilchrist[4)], reactive intermediates **2** are easily generated in situ by base treatment of the corresponding α-halogen oximes.

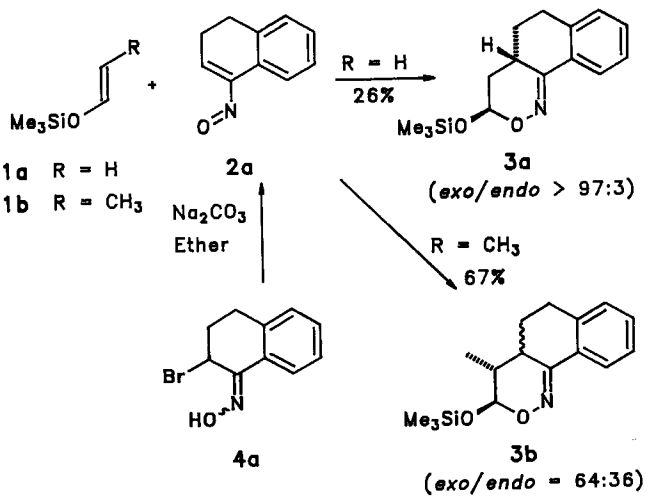


1 **2**

Characteristic features of this cycloaddition are high yields and a broad variability with respect to component **1**. For this reason it can serve as an ideal model reaction for the study of all relevant mechanistic details of a Diels-Alder reaction with inverse electron demand[5)]. Although several aspects have been investigated by Gilchrist and coworkers[6)], not all of their results are conclusive (e.g. stereospecificity of the cycloaddition). For the anticipated synthetic use[7)] of 1,2-oxazines, however, full understanding of the mechanism is an indispensable prerequisite. In this paper we will deal with the stereospecificity, the *exo/endo* and *E/Z* selectivity of nitroso alkenes as well as with the relative reactivity of silyl enol ethers **1**, or other suitable olefins, towards **2**.

exo/endo Selectivity of 3,4-Dihydro-1-nitrosonaphthalene

In an intramolecular nitroso alkene cycloaddition an *endo*-selective reaction has been reported (*exo:endo* = 1:3.4)[8)]. To study this stereochemical feature in the geometrically less restricted intermolecular reaction we have employed 3,4-dihydro-1-nitrosonaphthalene (**2a**). This compound incorporates an *E*-nitroso alkene moiety and is generated from the bromo oxime **4a**, which can easily be prepared from α-tetralone.

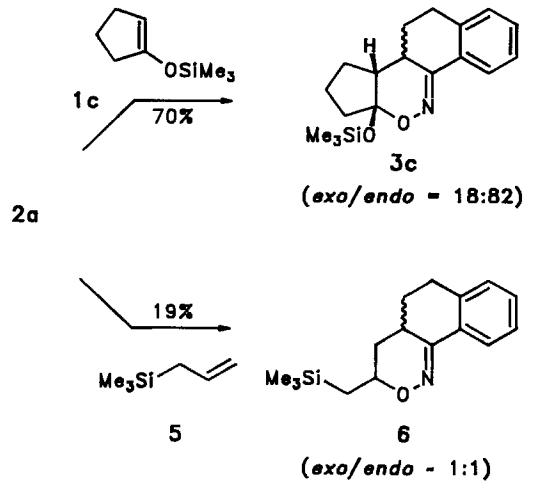


Cycloaddition of **2a** to trimethylsiloxy ethene (**1a**) affords *one* product whose spectroscopic data prove it to have structure **3a**. Proton 3-H exhibits coupling constants of 2 Hz, typical for a pseudo-equatorial position, whereas 4a-H and 4-H couple with J = 4 and 13 Hz, respectively, which is characteristic of a pseudo-axial location of this proton in

  0009–2940/90/1212–2403 $ 3.50+.25/0

the 1,2-oxazine ring. Assuming a half-chair conformation of this heterocycle, as is generally preferred[3], the drawn stereochemistry is inevitable. Thus, an exclusive *exo* addition of **2a** to **1a** has occured.

E-substituted olefin **1b** and **2a** provide a 64:36 mixture of two isomers of **3b**. Similar spectroscopic arguments as above prove that the *exo* adduct (with respect to the Me_3SiO group) is the major isomer. Experiments employing the corresponding *Z* olefin are not conclusive due to the low yield and instability of the cycloadducts isolated[2]. This is also true for the reaction of **2a** with cyclopentadiene, an otherwise excellent dienophile for nitroso alkenes[4]. However, 1-trimethylsiloxy cyclopentene (**1c**) and **2a** cleanly combine to provide 1,2-oxazine **3c** which incorporates an "azaoxasteroid" framework. The *exo/endo* ratio is 18:82. Finally, the cycloaddition of allylsilane **5** to nitroso alkene **2a** gives 1,2-oxazine **6** with an *exo/endo* ratio of approximately 1:1.

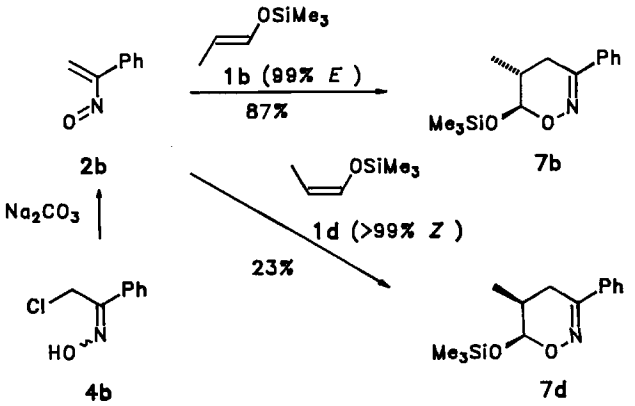


The reactions of heterodiene **2a** with silyl enol ethers reveal a clear trend: While **1a** undergoes exclusive *exo* addition, the introduction of one or two substituents as in **1b** and **1c**, disfavours this approach and leads to a dramatic increase in *endo* adducts. Comparison of reactions **1a** → **3a** and **1b** → **3b** reveals that a siloxy group displays a higher *exo*-directing effect than a methyl group. On the other hand, allylsilane **5**, which is sterically similar to **1a** at first glance, reacts unselectively with **2a**. We assume that conformational differences are important. While silyl enol ether **1a** should accommodate planar *s-trans* conformation **A**[9], a conformation **B** is more likely for allylsilane **5** according to MMX and MNDO calculations[10]. Here the Me_3Si-CH_2 bond occupies a position nearly perpendicular to the olefinic plane. However, due to the low yield of cycloadduct **6** and its tendency to decompose, the result of this reaction should not be overestimated.

The preference of nitroso alkenes for the *exo* approach has to be compared to the moderate to excellent *endo* selectivity observed for the related hetero Diels-Alder reactions of α,β-unsaturated carbonyl compounds with enol ethers[11-15]. In these examples stabilization of the *endo* approach by secondary orbital interactions was suggested[11a]. Apparently this effect is not decisive for nitroso alkenes. Since MO calculations[16] show close similarities between the frontier orbitals of both heterodienes, the structural reasons for these different reactivities are still unclear. Steric effects might be smaller in most α,β-unsaturated carbonyl compounds, since the β-substituents are H, CH_3, SC_6H_5, or COR[11-15], compared with the conformationally fixed aryl group in **2a**. On the other hand, a crucial effect might be due to the nitroso alkene's nitrogen lone pair. It could repel the oxygen atom of the dienophile in an *endo* approach. A quantum mechanical analysis of the transition states involved should help to understand these effects[17].

Stereospecificity of the Cycloaddition

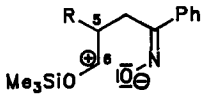
The concertedness previously suggested[6] for nitroso alkene cycloadditions has further been supported by the *E/Z*-isomeric pair of silyl enol ethers **1b** and **1d**. Isomerically very pure starting materials could be gained by *kinetic separation* of these olefins. We have exploited the high $k_{E/Z}$ value (see below) in the reaction of **2b** for purification of **1d**, whereas the high $k_{Z/E}$ ratio for the cycloaddition of diphenyl ketene allowed isolation of pure **1b**[18]. The isomerically homogeneous olefins have been treated with oxime **4b** and sodium carbonate to afford either 1,2-oxazine **7b** or **7d** via α-nitrosostyrene **2b**. According to HPLC and high-field NMR spectra of the crude products isolated, both cycloadducts have been obtained more than 99% isomerically pure. The considerably lower yield for **7d** is due to the rather moderate reactivity of **1d** (see below).



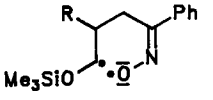
These results demonstrate stereospecificity of the cycloaddition. A concerted pathway to 1,2-oxazines is highly probable, since conceivable intermediates of a stepwise mechanism, either a 1,6-zwitterion **C** or a 1,6-diradical **D**, could undergo rotation around the C-5—C-6 bond and might therefore give isomeric mixtures of **7**.

In all experiments described in this account, mixtures of *E/Z*-isomeric oxime **4b** served as precursor for nitroso alkene **2b**. While *Z*-**4b** directly provides *s-cis*-**2b** capable of performing the (concerted) cycloaddition with **1b** and **1d**,

the corresponding *E*-**4b** must give primarily *s-trans*-**2b**. This conformer can either be transformed into *s-cis*-**2b** or it can add to **1b** giving intermediate **E** (or the corresponding diradical). Faster rotation around the C-5–C-6 bond in **E** than around the C–N bond is very likely[6a]. Therefore, the observation of stereospecific formation of **7b** and **7d**, respectively, with *E*-**4b** as starting material further argues against the possibility of a stepwise mechanism.

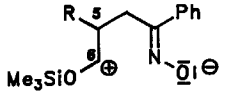


C



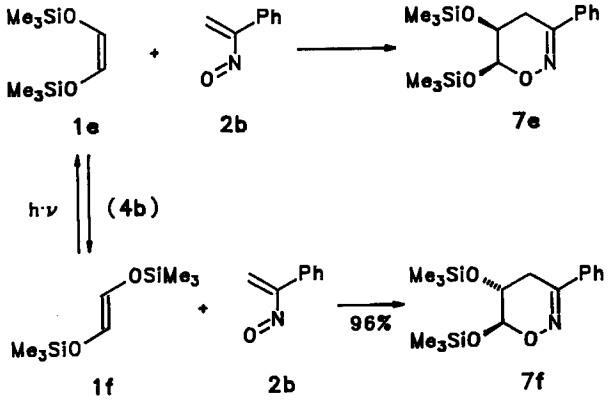
D

s-trans-**2b**



E

An apparently nonstereospecific cycloaddition has been observed with *cis* olefin **1e**! Pure **1e** provides a 60:40 mixture of **7e** and **7f** in rather low yield (25%). The coupling patterns in the ^{1}H-NMR spectra demonstrate that both siloxy groups in **7f** are axially situated (*trans* stereochemistry), while for the *cis*-1,2-oxazine **7e** only the 6-siloxy group is located in an axial position. On the other hand, when a large excess of a 1:1 mixture of **1e** and **1f** – as obtained by photochemical equilibration[19] – was treated with **2b**, pure *trans*-1,2-oxazine **7f** was formed exclusively, in excellent yield.



1e **2b** **7e**

1f **2b** **7f**

This puzzling result, in that the isomerically pure olefin gives two diastereomeric cycloadducts whereas a mixture of *E*/*Z* olefins provides a homogeneous 1,2-oxazine, is consistently interpreted as follows:

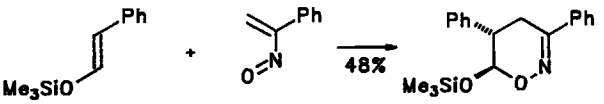
a) the [4 + 2] cycloaddition of **1f** is stereospecific.

b) the *E* olefin **1f** cycloadds much faster to **2b** than the *Z* alkene **1e** ($k_{E/Z} > 50$); this preference for *E* olefins is generally observed for nitroso alkenes (see below).

c) since *Z* olefin **1e** reacts very slowly with **2b**, isomerization of **1e** to give **1f** can compete, thus providing the precursor for *trans*-1,2-oxazine **7f**.

Under the conditions of the cycloaddition, the proposed *Z*/*E* isomerization was not observed for other silyl enol ethers. However, the 1,2-bis(siloxy)ethene **1e** should be much more basic than enol ethers with one siloxy group: A proton-catalyzed *cis*/*trans* equilibration – with **4b** serving as proton source, for instance – is hence conceivable. An epimerization of the cycloadducts **7e** or **7f** was excluded by control experiments[2].

A stereospecific [4 + 2] cycloaddition of nitroso alkene **2b** has also been found when the β-siloxystyrene **1g** was used as dienophile. Again, an *E*/*Z* mixture of olefins (**1g** and **1h**) has been used as starting compounds, but only the *trans*-substituted olefin **1g** reacts with **2b** to give cycloadduct **7g** exclusively[18]. In addition to its stereospecificity, it is important to realize the complete regioselectivity of this reaction. A cycloaddition passing a radical or radicaloid intermediate similar to **D** is not expected to be regioselective in the case of **1g**. The phenyl group should exhibit a better radical stabilization than $OSiMe_3$[20] and the opposite regiochemistry should be preferred.



1g (+ **1h**) **2b** **7g**

All experiments described in this paragraph support a stereospecific and concerted mechanism[21] for this cycloaddition[22]. Gilchrist has also interpreted the stereospecific reactions of a nitroso alkene with *E*- and *Z*-cyclooctene as evidence that no long-lived intermediates are involved[6]. Stereospecificity has also been assumed or experimentally demonstrated for the related hetero Diels-Alder reactions of α,β-unsaturated carbonyl compounds[12-15,23]. However, recent theoretical work has questioned the concertedness of these cycloadditions[24], and for reactions of isoquinolinium salts to enol ethers a stereospecific but stepwise mechanism has been suggested[25].

E/*Z* Selectivity of Nitroso Alkenes

During our synthetic investigations[3] we have realized that α-nitroso styrene **2b** reacts much faster with *E* olefin **1b** than with the corresponding *Z* isomer **1d**. This behaviour could be exploited for a very convenient kinetic separation of *E*/*Z*-isomeric silyl enol ethers[18]. The higher reactivity of *E* olefins towards nitroso alkenes has already been noted by Gilchrist but the effect was not quantified[6a]. We therefore have performed competition experiments (equation 1) and determinded $k_{E/Z}$ as given in Table 1. The accuracy of these values should not be overestimated since partial decomposition (or loss) of the produced 1,2-oxazines can falsify the result. However, the error should be below ± 20% for the competition constant $k_{E/Z}$ (see Experimental).

Thus, for the pair **1b**/**1d**, $k_{E/Z}$ has been determined to be 26. While the β-isopropyl-substituted alkenes **1i**/**1j** have a similar competition constant, the β-phenyl- or β-trimethylsiloxy-substituted silyl enol ethers **1g**/**1h** or **1f**/**1e** are even more selective. In these experiments only the *E* isomers react to furnish the *trans* cycloadducts **7g** and **7f** exclusively. On

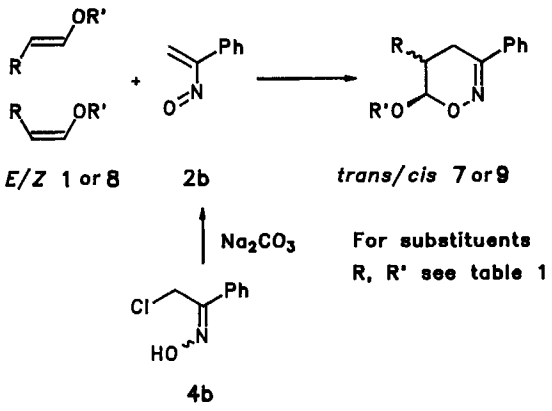
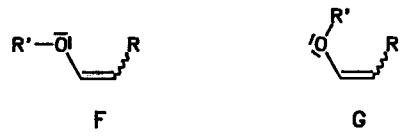


Table 1. Competition experiments employing *E*/*Z*-isomeric olefins and α-nitrososty rene **2b** according to equation (1)

Olefins *E/Z*	R	R'	Products *trans / cis*	$k_{E/Z}$
1b / 1d	Me	$SiMe_3$	**7b / 7d**	26
1i / 1j	i-Prop	$SiMe_3$	**7i / 7j**	25
1g / 1h	Ph	$SiMe_3$	**7g / -**	> 50
1f / 1e	$OSiMe_3$	$SiMe_3$	**7f / -**	> 50
8a / 8b	Me	Et	**9a / 9b**	6

the other hand, a considerably lower competition constant of 6 has been found for the isomeric pair of ethyl 1-propenyl ether (**8a/8b**). The higher reactivity of *E* olefins with respect to their corresponding *Z* isomers in [4 + 2] and [3 + 2] cycloadditions is a rather general observation[26–28] although it is still not very well understood. In general, the major argument proposes that an optimal conjugation of substituents in *Z* olefins is prevented by steric repulsion. These isomers are therefore electronically less activated than the *E* alkenes. It must be emphasized that for a given pair of isomers the magnitude of $k_{E/Z}$ is highly dependent on the reaction performed[26–28]. This has also been confirmed for silyl enol ethers **1b/1d**, whose discrimination is considerably lower in other cycloadditions[29] than in the hetero Diels-Alder reactions described here.

The argument for diminished electronic activation looks reasonable for the β-isopropyl-, β-phenyl-, and β-trimethylsiloxy-substituted olefins **1i/1j**, **1g/1h**, and **1f/1e**, although the magnitude of the effect is rather unexpected[30]. But for sterically less hindered *E*/*Z*-isomeric enol ethers, severe electronic differences in the ground state are not evident. The ionization potentials of **8a** and **8b** – which can be taken as a measure for the HOMO energy of these olefins – are almost identical[31]. The ^{13}C-NMR data of siloxypropenes **1b/1d** and ethoxypropenes **8a/b** also reveal only minor differences, an indication that the charge densities at the olefinic carbons are rather similar. The interpretation of enol ether reactivities is complicated by the possible influence of different conformations. Thus for silyl enol ethers the *s-trans* location of the siloxy function should be more stable for both stereoisomers (see **F**)[9a]. The electronically more favourable and stronger activating *s-cis* conformation **G** can be adopted at least in the *E* alkyl enol ether **8b**[9b-e].



F G

Possibly this conformational difference is in part responsible for the higher reactivity of alkyl enol ethers over the corresponding silyl enol ethers (see below), but none of these effects provide a satisfactory explanation for the rather high $k_{E/Z}$ values of siloxypropenes **1b/1d** and the remarkably lower discrimination of ethoxypropenes **8a/8b**[32]. However, whatever the reason for the high $k_{E/Z}$ selectivity observed may be, it is a strong argument against the participation of dipolar intermediates in these [4 + 2] cycloadditions. The reactions of tetracyanoethylene with *E*/*Z*-isomeric enol ethers[33] – the most prominent examples for two-step [2 + 2] cycloadditions – reveal $k_{E/Z}$ ratios of approximately 1.

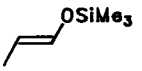
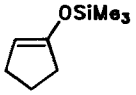
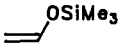
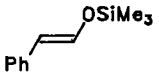
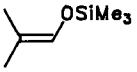
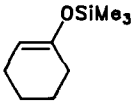
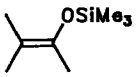
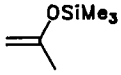
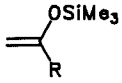
Relative Reactivities of Silyl Enol Ethers and Other Olefins

Having found these pronounced reactivity differences for rather similar dienophiles, we have extended the competition experiments to various structurally differing silyl enol ethers and other typical dienophiles. Thus, a scale of relative reactivities of olefins towards α-nitrososty rene **2b** could be drawn up with trimethylsiloxyethene (**1a**) serving as standard (k_{rel} = 100). Scheme 1 shows that a delicate balance of electronic and steric effects determines the rate of the [4 + 2] cycloadditions. β-Substituents *trans* to the siloxy group increase the reactivity, while *cis*-positioned groups lower the rate (see Table 1). Most intriguing is the effect of α-substituents, which strongly *decelerate* the cycloaddition. For example, the 2-siloxy-1-propene **1n** reacts very slowly and the related silyl enol ethers with an isopropyl, *tert*-butyl, or phenyl group at the α-carbon do not react at all with the hetero diene **2b**[34]. Since these substituents are able to stabilize a positive charge (or a radical) in a possible intermediate or in the transition state of the cycloaddition, their electronic effect is apparently not very relevant, and is outweighed by their steric influence.

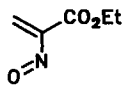
The competition between standard olefin **1a** and β-disubstituted silyl enol ether **1k** has also been executed with the more reactive nitroso alkenes **2c** and **2d**. The $k_{1a/1k}$ values are similar to that of **2b** and in the range of 3–4[2]. Therefore, the structure of the nitroso alkene is of minor influence for this pair of olefins.

To fully explore the reactivity pattern of **2b** we included a few other typical olefins in the rate studies. As illustrated in Scheme 2, cyclopentadiene **10** is almost as reactive as silyl enol ether **1b** (Scheme 1), while allyltrimethylsilane is at the end of the scale.

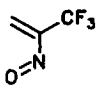
Scheme 1

Silyl Enol Ether		k_{rel} towards **2b** [room temp., Et_2O]
	**1b**	1150
	**1c**	220
	**1a**	100
	**1g**	95
	**1k**	33
	**1l**	19
	**1m**	13
	**1n**	11
	R = i-Prop, Ph, tert-Bu	< 1

Ethoxyethene (**11**) reacts about three times faster than the corresponding silicon compound **1a**. A similar ratio has been found for 1-ethoxycyclohexene (**13**) and 1-(trimethylsiloxy)cyclohexene (**1l**). It is also interesting to realize that methoxyallene (**12**) – a synthetically extremely useful dienophile[35,15a] – fits into the scheme, as it is slightly less reactive than ethyl vinyl ether (**11**). The results show that the activating ability of substituents follows the expected order EtO > Me_3SiO > Me_3SiCH_2.



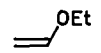
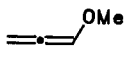
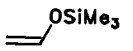
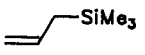
2c



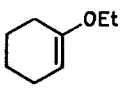
2d

Christl and Henneberger have compared the relative rates of **2b** towards cyclopentadiene, benzvalene, and norbornene[36]. Adapted to our scale with cyclopentadiene as linking dienophile, the strained olefins would provide k_{rel} = 1700 (benzvalene) and 9 (norbornene), emphasizing the exceptional behavior of strained olefins[37]. It should also be noted that no rearrangement products could be detected in these cycloadditions[36,3], which are possible when carbenium ions as intermediates are involved.

Scheme 2

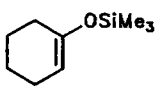
		k_{rel} towards **2b** [room temp., Et_2O]
	**10**	850
	**11**	350
	**12**	120
	**1a**	100
	**5**	20

The reactivity pattern of **2b** with various olefins is rather different from that of protons with enol ethers[38] and of carbenium ions with (silyl) enol ethers, allylsilanes, or other olefins[39]. This again indicates that carbenium ions **C** or **E** are not involved as intermediates. The rate of the [4 + 2] cycloaddition of heterodiene **2b** with olefins is mainly governed by the electron density of the dienophile (HOMO energy), though a correlation with their ionization potentials is not achievable due to the lack of data for silyl enol ethers. Also, the great importance of steric effects would hardly allow a good correlation. On the other hand, we take these as further evidence for the concertedness of the [4 + 2] cycloadditions under discussion. A highly ordered transition state may be responsible for the large influence of steric effects demonstrated for the *exo/endo* and $k_{E/Z}$ selectivity, and in the reactivity pattern.



13

$k_{13} \sim 3 \cdot k_{11}$



11

Final Mechanistic Conclusions

Taken alone, none of the experiments described in this paper would provide unequivocal arguments for the concerted mechanism of nitroso alkene cycloadditions. However, as a whole the many facets of this reaction provide a convincing picture that the usual pathway is a concerted one. This statement surpasses Gilchrist's conclusion that no

Table 2. Synthesis of 1,2-oxazines **3a–c** and **6** from oxime **4a**

Oxime **4a** g (mmol)	Olefin	g (mmol)	Time (h)	Product	Yield g (%)	exo:endo
1.20 (5.00)	**1a**	2.91 (25.0)	76	**3a**	0.350 (26)	> 97:3
0.480 (2.00)	**1b**[a]	5.21 (40.0)	72	**3b**	0.386 (67)	64:36
2.40 (10.0)	**1c**	7.82 (50.0)	216	**3c**	2.20 (70)	18:82
2.40 (10.0)	**5**	5.71 (50.0)	72	**6**	0.531 (19)	50:50

[a] A mixture of **1b**/**1d** (25:75) was used; only the *E* isomer reacts with **2a**.

long-lived intermediate is involved in this example of a Diels-Alder reaction with inverse electron demand[6a]. Nevertheless, the transition state of this [4 + 2] cycloaddition may be rather unsymmetric, with a more advanced C–C bond formation compared to the C–O bond closure. The PM3 calculations of Sustmann strongly support this claim[17]. In extreme situations the reaction pathway may involve 1,6-zwitterions. For a sterically highly hindered allene derivative we have good evidence for this two-step mechanism[22]. However, for (silyl) enol ethers there are no indications for the participation of intermediates. The firm mechanistic basis laid in this study will help to fully explore the synthetic potential of 1,2-oxazines.

Financial support by the *Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie*, and the *Vereinigung von Freunden der Technischen Hochschule zu Darmstadt* is gratefully appreciated. We thank Prof. Dr. *R. Sustmann* (Universität-Gesamthochschule Essen) for discussions and his kind readiness to perform PM3 calculations. Constructive discussions with Prof. Dr. *H. Mayr* (Medizinische Universität Lübeck) as well as submission of unpublished material by Prof. Dr. *J. Sauer* (Universität Regensburg) and Prof. Dr. *M. Christl* (Universität Würzburg) are gratefully acknowledged. We also thank Prof. Dr. *H.-D. Scharf* (Rheinisch-Westfälische Technische Hochschule Aachen) for a generous gift of compound **1e**.

Experimental

For general remarks and characterization of 1,2-oxazines **7** see ref.[3].

Reactions of 3,4-Dihydro-1-nitrosonaphthalene **2a**. – *General Procedure:* A solution of oxime **4a** and the corresponding olefin (5

Table 3. Analytical data for 4-substituted 4,4a,5,6-tetrahydro-3-trimethylsiloxy-3*H*-naphtho[1,2-*c*][1,2]oxazines **3a–c** and **6**

Compound	IR (cm^{-1})	Elemental Analysis	C	H	N
3a	(film) 3100-3000, 2990-2800 (C-H), 1610 (C=N)	$C_{15}H_{21}NO_2Si$ (275.4)			
		Calcd.	65.41	7.69	5.09
		Found	65.82	7.76	4.82
3b	(film) 3100-3000, 2990-2800 (C-H), 1610 (C=N)	$C_{16}H_{23}NO_2Si$ (289.5)			
		Calcd.	66.39	8.01	4.84
		Found	66.79	8.11	4.65
3c	(KBr) 3100-3000, 2995-2750 (C-H), 1610 (C=N)	$C_{18}H_{25}NO_2Si$ (315.5)			
		Calcd.	68.53	7.99	4.44
		Found	68.68	8.34	4.40
6	(film) 3100-3000, 2990-2850 (C-H), 1605 (C=N)	$C_{16}H_{23}NOSi$ (273.5)			
		Calcd.	70.28	8.48	5.12
		Found	69.91	8.03	5.11

[a] All compounds except **3c** (m.p. 48–54 °C) are colorless liquids.

Table 4. ^{1}H-NMR data of 1,2-oxazines **3a–c** and **6** (300 MHz, $CDCl_3$, δ values)[a]

Compound	3-H (1 H) d[b]	6-H (2 H) m_c[b]	4a-H (1 H) ddd[b]	4-H (1 H) m_c[b]	5-H (2 H) m_c[b]	Other Signals	$SiMe_3$ (9H) s
3a	5.55 t (2)	2.86	2.61 ddt (4, 6.5, 13)	1.91 1.62 dt (2,13)[c]	1.91 m_c 1.55 dq (5.5, 13)	–	0.16
exo-**3b**	5.22 (2)	2.86	2.82 (4.5, 6.5,13)	1.99	1.79	0.88 (d, *J* = 7 Hz, 3 H, Me)	0.24
endo-**3b**	4.90 (8)	2.86	2.24 (3, 8, 13)	2.03	1.66	1.07 (d, *J* = 7 Hz, 3 H, Me)	0.23
exo-**3c**	–	2.77	2.58 (4.5, 6.5, 13)	2.03	1.90	2.0-1.2 m (6 H)	0.15
endo-**3c**	–	2.77	2.43 (4, 6.5, 13)	[d]	[d]	[d]	0.10
6	3.91 m_c	2.81	2.35 m_c	[e]	[e]	1.07, 0.77, (dd, m_c, *J* = 7.5, 14 Hz, 2 H, $\underline{CH_2}SiMe_3$)	0.15 0.08

[a] All compounds δ = 8.0–7.8, 7.4–7.0 (2 m, 1 H, 3 H, C_6H_4). – [b] Multiplicity of the signal if not indicated; values in parentheses: coupling constants in Hz. – [c] 2 H. – [d] Signals hidden by the multiplet (δ = 2.0–1.2). – [e] Signals hidden by the multiplet (δ = 2.0–1.3).

Table 5. ^{13}C-NMR data of 1,2-oxazines **3a–c** and **6** ($CDCl_3$, δ values)[a]

Compound	C-10b s	C-3 d	C-4 d	C-5 C-6 2t	C-4a d	Other Signals	$SiMe_3$ q
3a	154.8	91.4	38.5[b][c]	31.9, 28.9[c]	25.2	--	0.0
exo-**3b**	153.0	96.1	40.0	29.3, 24.4	29.5	11.9 (q, Me)	0.0
endo-**3b**	155.1	99.2	37.7	27.1, 24.4	32.7	14.4 (q, Me)	0.2
exo-**3c**	163.8	109.8[d]	51.1	31.0, 29.1[c]	35.9	40.9, 27.2, 22.7[c] (3 t, 3 CH_2)	1.3
endo-**3c**	151.8	105.8[d]	42.8	29.2, 25.8[c]	37.2	32.2, 23.4, 19.6[c] (3 t, 3 CH_2)	1.1
exo-**6**[e]	157.8	72.7	35.8[b]	30.1, 29.2	29.0	22.5 (t, CH_2Si)	-0.8
endo-**6**[e]	153.7	74.9	35.1[b]	30.1, 29.1	35.6	23.4 (t, CH_2Si)	-0.6

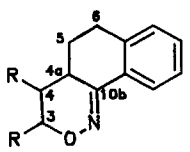
[a] For all compounds: δ = 138.5–130.8, 2 s, 129.6–125.4, 4 d, C_6H_4. – [b] Triplet. – [c] Assignment uncertain; marked values are exchangeable. – [d] Singlet. – [e] Assignment uncertain; values are exchangeable with those of the second isomer.

Table 6. Competition experiments with *E/Z*-isomeric olefins in diethyl ether at room temperature (according to the general procedure)[a]

Oxime g (mmol)	*E/Z*-Olefins (mmol) Ratio		Time (h)	Products[b] (*trans:cis*)	Yield g (%)	k_{comp}
4b	**1b**	**1d**	144	**7b / 7d**	0.416	26
0.340	(11.0)	(39.0)		(88:12)	(79)	
(2.00)	22:78					
4b	**8a**	**8b**	96	**9a / 9b**	0.43[d]	6
0.340	(9.3)	(27.7)		(68:32)	(98)	
(2.00)	25:75					
4b	**1i**	**1j**	41	**7i / 7j**	0.70	25
0.85	(8.8)	(16.2)		(93:7)	(48)	
(5.00)	35:65					

[a] Experiment for **1b/1d** + **4a** included in Table 2. – [b] Ratio of the crude products. – [c] Yield of the crude product mixture analyzed. – [d] Yield of the purified cycloadduct; for characterization see below.

equivalents) in diethyl ether (20 ml/mmol of **4a**) was stirred with freshly ground sodium carbonate (10 equivalents) for the time indicated in Table 2 at room temperature. The suspension was filtered through a pad of Celite (elution with dichloromethane), and the crude product obtained after evaporation was further purified by chromatography (Al_2O_3, pentane/ethyl acetate = 4:1) or recrystallization. For characterization of compounds **3a–c** and **6** see Tables 3–5.



Stereospecificity: A solution of 0.850 g (5.00 mmol) of oxime **4b** and 3.25 g (25.0 mmol) of **1b** (99% pure according to HPLC) in 100 ml of diethyl ether was stirred with 5.30 g (50.0 mmol) of sodium carbonate for 72 h at room temperature. Filtration through a pad of Celite, elution with dichloromethane, and evaporation of the solvents provided 1.14 g (87%) of **7b** as a colorless oil. The compound was >99% isomerically pure according to HPLC and ^{1}H-NMR spectroscopy (300 MHz).

Analogously to the preceding experiment, 0.425 g (2.50 mmol) of **4b**, 1.63 g (12.5 mmol) of **1d** (>99% pure according to GC and HPLC), and 5.30 g (50.0 mmol) of Na_2CO_3 in 100 ml of diethyl ether was stirred for 72 h at room temperature and filtered to afford 0.164 g (25%) of **7d** as colorless crystals (m.p. 34–35°C). The cycloadduct was >99% isomerically pure according to HPLC and ^{1}H-NMR spectroscopy (300 MHz).

Analogously to the reaction with **1b**, 0.850 g (5.00 mmol) of **4b**, 5.10 g (25.0 mmol) of **1e** (>97% pure according to ^{1}H NMR), and 6.36 g (30.0 mmol) of Na_2CO_3 (added in two portions) in 100 ml of diethyl ether was stirred for 120 h at room temperature and filtered to afford 0.379 g (23%) of **7e/7f** (60:40) as colorless crystals (m.p. 70–80°C). – NMR data for **7e**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.60, 7.38 (2 m_c, 2H, 3H, C_6H_5), 5.31 (d, J = 2.5 Hz, 1H, 6-H), 4.16 (ddd, J = 2.5, 7, 10 Hz, 1H, 5-H), AB part of ABX (δ_A = 2.72, δ_B = 2.64, J_{AB} = 17 Hz, J_{AX} = 10 Hz, J_{BX} = 7 Hz, 2H, 4-H_{ax}, 4-H_{eq}), 0.20, 0.19 (2 s, 18H, $OSiMe_3$). – ^{13}C NMR ($CDCl_3$): δ = 154.6 (s, C-3), 136.0, 129.5, 129.3, 125.6 (s, 3 d, C_6H_5), 93.0 (d, C-6), 64.5 (d, C-5), 27.0 (t, C-4), 0.19, 0.08 (2 q, $OSiMe_3$).

For the synthesis of *trans*-1,2-oxazines **7f** and **7g** from **1e/1f** and **1g** as well as full characterization of these compounds see ref.[3].

Competition Experiments. – General Procedure: A solution of the oxime **4** and the mixture of the corresponding olefins in diethyl ether (20 ml/mmol of **4**) was stirred with freshly ground sodium carbonate (10 equivalents) at room temperature. The individual component ratios and the reaction times are recorded in Tables 6 and 7. For workup the suspension was filtered through a short pad of Al_2O_3 and the filtrate was analyzed by HPLC (column: Nucleosil 100, 5 μ; pressure: 12–13 MPa; elution: hexane/ethyl acetate, 98:2) or by ^{1}H-NMR spectroscopy. The identification was confirmed by comparison with the signals of pure 1,2-oxazines obtained after further purification and/or separation of the products (see ref.[3]).

Table 7. Competition experiments with various olefins in diethyl ether at room temperature (according to the general procedure)[a]

Oxime **4b** g (mmol)	Olefins (mmol)		Time (h)	Products[b]	Yield g (%)	k_{comp}
0.340 (2.00)	**1a** (10.0)	**1b**[c] (10.0)	96	**7a / 7b** (8:92)	0.312 (59)	0.087
0.340 (2.00)	**1a** (10.0)	**1k** (10.0)	72	**7a / 7k** (75:25)	0.182 (36)	3.0
0.340 (2.00)	**1a** (10.0)	**1n** (10.0)	72	**7a / 7n** (90:10)	0.182 (36)	9.0
0.510 (3.00)	**1a** (15.0)	**1g** (15.0)	120	**7a / 7g** (51:49)	0.622 (72)	1.04
0.340 (2.00)	**1a** (10.0)	**1l** (10.0)	120	**7a / 7l** (84:16)	0.187 (39)	5.25
0.850 (5.00)	**1k** (25.0)	**1m** (25.0)	96	**7k / 7m** (72:28)	1.26 (90)	2.57
0.340 (2.00)	**1c** (10.0)	**1l** (10.0)	96	**7c / 7l** (92:8)	0.389 (67)	11.5
0.680 (4.00)	**10** (20.0)	**11** (20.0)	96	**ca-10 / ca-11** (70:30)	0.705 (88)	2.33
0.850 (5.00)	**11** (25.0)	**1a** (25.0)	72	**ca-11 / 7a** (78:22)	0.927 (86)	3.55
0.850 (5.00)	**13** (25.0)	**1l** (25.0)	56	**ca-13 / 7l** (75:25)	0.840 (62)	3.00
0.850 (5.00)	**11** (25.0)	**12** (25.0)	72	**ca-11/ ca-12** (74:26)	0.840 (82)	2.85
0.338 (2.00)	**5** (10.0)	**1m** (10.0)	96	**ca-5 / 7m** (66:34)	0.245 (47)	1.94

[a] Product ratios and yields refer to the crude product mixture; all individual adducts are characterized in ref.[3]. — [b] **ca-10, ca-11**, ... means cycloadduct of **10, 11**, ...; for full characterization of these 1,2-oxazines see ref.[3,4,6,35]. — [c] 6.19 g (47.6 mmol) of **1b/1d** have been used (**1b**:**1d** = 21:79).

The competition constants k_{comp} as given in Tables 6 and 7 are calculated according to the following approximation[40]:

$$k_{comp} = \frac{[\text{olefin II}] \cdot [\text{cycloadduct I}]}{[\text{olefin I}] \cdot [\text{cycloadduct II}]}$$

This equation is valid for a large excess of olefins. Experiments performed with moderate excess of one olefin component (<2 equivalents with respect to oxime **4**) allow only a very crude approximation of k_{comp}. The error in individual competition experiments is estimated to be 10–20%, due to the possible differences in stability between 1,2-oxazines. The analytical accuracy should be 3–5% (NMR or HPLC).

cis/trans-6-Ethoxy-5,6-dihydro-5-methyl-3-phenyl-4H-1,2-oxazine (**9a/b**): For preparation and yield see Table 6. — ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73–7.69, 7.39–7.37 (2 m, 2H, 3H, Ph), 4.96 (d, J = 2.5 Hz, 0.32H, 6-H, *cis*), 4.82 (d, J = 2.5 Hz, 0.68H, 6-H, *trans*), 3.91, 3.63, 1.20 (3 m_c, 1H, 1H, 3H, OCH_2CH_3), 2.85 (dd, J = 7.5/18 Hz, 0.68H, 4-H_a, *trans*), 2.49, 2.37 (AB part of ABX, J_{AB} = 18 Hz, J_{AX} = 6.5 Hz, J_{BX} = 11 Hz, 0.64H, 4-H_e, 4-H_a, *cis*), 2.23–2.16 (m, 1.68H, 4-H_e, *trans*, 5-H), 1.11, 1.06 (2 d, J = 6.5/7 Hz, 3H, 5-CH_3).

$C_{13}H_{17}NO_2$ (219.3) Calcd. C 71.20 H 7.81 N 6.39
Found C 70.95 H 7.95 N 6.20

CAS Registry Numbers

1a: 6213-94-1 / **1b**: 39162-68-0 / **1c**: 19980-43-9 / **1d**: 50300-18-0 / **1g**: 35449-05-9 / **1i**: 73397-84-9 / **1j**: 73397-85-0 / **1k**: 6651-34-9 / **1l**: 6651-36-1 / **1m**: 17510-44-0 / **1n**: 1833-53-0 / *exo*-**3a**: 128388-76-1 / *exo*-**3b**: 128388-77-2 / *endo*-**3b**: 128443-31-2 / *exo*-**3c**: 128443-32-3 / *endo*-**3c**: 128443-33-4 / **4a**: 56384-59-9 / **4b**: 21572-32-7 / **5**: 762-72-1 / **ca-5**: 109925-98-6 / *exo*-**6**: 128388-78-3 / *endo*-**6**: 128388-79-4 / **7a**: 124462-47-1 / **7b**: 125173-09-3 / **7c**: 124462-58-4 / **7d**: 125173-08-2 / **7e**: 128388-80-7 / **7f**: 124481-51-2 / **7g**: 124462-54-0 / **7i**: 124462-51-7 / **7j**: 124462-50-6 / **7k**: 109925-93-1 / **7l**: 109925-95-3 / **7m**: 124462-55-1 / **7n**: 109925-96-4 / **8a**: 4696-26-8 / **8b**: 4696-25-7 / **9a**: 128388-81-8 / **9b**: 128388-82-9 / **10**: 542-92-7 / **ca-10**: 61145-16-2 / **11**: 109-92-2 / **ca-11**: 80322-70-9 / **12**: 13169-00-1 / **ca-12**: 117341-58-9 / **13**: 1122-84-5 / **ca-13**: 124462-39-1

[1] Dedicated to Professor *Rolf Huisgen* on the occasion of his 70th birthday.
[2] C. Hippeli, *Dissertation*, Technische Hochschule Darmstadt, 1989.
[3] C. Hippeli, H.-U. Reißig, *Liebigs Ann. Chem.* **1990**, 217.
[4] [4a] R. Faragher, T. L. Gilchrist, J. Chem. Soc., *Perkin Trans. 1*, **1979**, 249. — [4b] T. L. Gilchrist, *Chem. Soc. Rev.* **12** (1983) 53.
[5] [5a] W. E. Bachmann, N. C. Deno, *J. Am. Chem. Soc.* **71** (1949) 3062; J. Sauer, H. Wiest, *Angew. Chem.* **79** (1967) 76; *Angew. Chem. Int. Ed. Engl.* **6** (1967) 16. — [5b] Reviews: D. L. Boger, S. N. Weinreb, *Hetero Diels-Alder, Methodology in Organic Synthesis*, Academic Press, New York, 1987; D. L. Boger, *Tetrahedron* **39** (1983) 2869.
[6] [6a] D. E. Davies, T. L. Gilchrist, T. G. Roberts, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1275. — [6b] T. L. Gilchrist, T. G. Roberts, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1283.
[7] For recent examples see: E. J. T. Chrystal, T. L. Gilchrist, W. Stretch, *J. Chem. Res. (S)* **1987**, 180; *J. Chem. Res. (M)* **1987**, 1563. — R. Plate, P. H. H. Hermkens, H. Behm, H. C. J. Ottenheijm, *J. Org. Chem.* **52** (1987) 560. — R. Henning, U. Lerch, H. Urbach, *Synthesis* **1989**, 265. — C. Hippeli, R. Zimmer, H.-U. Reißig, *Liebigs Ann. Chem.* **1990**, 469. — C. Hippeli, H.-U. Reißig, *Liebigs Ann. Chem.* **1990**, 475.
[8] S. E. Denmark, M. S. Dappen, J. Org. Chem. **49** (1984) 798.
[9] [9a] A. N. Lazarev, I. S. Ignat'ev, L. L. Schukovskaya, R. I. Pal-'chik, *Spectrochim. Acta Part A*, **27** (1971) 2291. — For theoretical and experimental work on the conformation of alkyl enol ethers see: [9b] F. Bernardi, N. D. Epiotis, R. L. Yates, H. B. Schlegel, *J. Am. Chem. Soc.* **98** (1976) 2385. — [9c] E. Taskinen, E. Kukkamäki, H. Kotilainen, *Tetrahedron* **34** (1978) 1203. — [9d] H. Friege, M. Klessinger, *Chem. Ber.* **112** (1979) 1614. — [9e] D. Bond, P. v. R. Schleyer, *J. Org. Chem.* **55** (1990) 1003, and ref. cited therein.
[10] H.-U. Reißig, unpublished calculations. For the MINDO/3 calculation of (3-methyl-3-butenyl)trimethylsilane see: G. Déléris, J. P. Pillot, J. C. Rayez, *Tetrahedron* **36** (1980) 2215.
[11] [11a] G. Desimoni, C. Colombo, P. P. Righetti, G. Tacconi, *Tetrahedron* **29** (1973) 2635. — [11b] Review: G. Desimoni, G. Tacconi, *Chem. Rev.* **75** (1975) 651.
[12] B. B. Snider, *Tetrahedron Lett.* **21** (1980) 1133.
[13] [13a] M. Maier, R. R. Schmidt, *Liebigs Ann. Chem.* **1985**, 2261. — [13b] S. Apparao, M. E. Maier, R. R. Schmidt, *Synthesis* **1987**, 900. — [13c] B. Haag-Zeino, M. E. Maier, R. R. Schmidt, *Chem. Ber.* **120** (1987) 1505. — [13d] R. R. Schmidt, B. Haag-Zeino, M. Hoch, *Liebigs Ann. Chem.* **1988**, 885. — [13e] Review: R. R. Schmidt, *Pure Appl. Chem.* **59** (1987) 415.

[14] [14a] L.-F. Tietze, K.-H. Glüsenkamp, K. Harms, G. Remberg, G. M. Sheldrick, *Tetrahedron Lett.* **23** (1982) 1147. – [14b] L.-F. Tietze, E. Voß, K. Harms, G. M. Sheldrick, *ibid.* **26** (1985) 5273. – [14c] L.-F. Tietze, E. Voß, *ibid.* **27** (1986) 6181. – [14d] L.-F. Tietze, J. Bachmann, W. Schul, *Angew. Chem.* **100** (1988) 983; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 971. – [14e] L.-F. Tietze, U. Hartfiel, *Tetrahedron Lett.* **31** (1990) 1697.

[15] [15a] D. L. Boger, K. D. Robarge, *J. Org. Chem.* **53** (1988) 3373. – [15b] M. Hojo, R. Masuda, E. Okada, *Synthesis* **1990**, 347.

[16] For a CNDO/2 calculation of nitrosoethylene see ref.[4a], for those of acrolein see: K. N. Houk, R. W. Strozier, *J. Am. Chem. Soc.* **95** (1973) 4094.

[17] A calculation of the *exo/endo* transition states by the PM3 method reveals no clear effect. Though a modest preference for the *exo* approach was found the difference in energy is too small to be significant (Prof. R. Sustmann, Universität-Gesamthochschule Essen, private communication).

[18] C. Hippeli, N. Basso, F. Dammast, H.-U. Reißig, *Synthesis* **1990**, 26.

[19] H.-D. Scharf, J. Mattay, *Tetrahedron Lett.* **1976**, 3509.

[20] B. Giese in *C-Radikale in Methoden der Organischen Chemie* (Houben-Weyl), 4th ed., vol. E 19a (M. Regitz, B. Giese, Eds.) p. 22, Thieme-Verlag, Stuttgart, 1989.

[21] For a detailed discussion of the criterium of stereospecificity see: [21a] J. Sauer, R. Sustmann, *Angew. Chem.* **92** (1980) 773; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 779. – [21b] R. Huisgen, *Advances in Cycloaddition*, **1** (1988) 1.

[22] Reaction of **2b** with 1-hydroxy-2-methoxy-1,1-diphenyl-2,3-butadiene provides a cycloadduct which was probably generated via a dipolar intermediate: R. Zimmer, H.-U. Reißig, unpublished results.

[23] A. B. Padias, S. T. Hedrick, H. K. Hall, Jr., *J. Org. Chem.* **48** (1983) 3787.

[24] L.-F. Tietze, J. Fennen, E. Anders, *Angew. Chem.* **101** (1989) 1420; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 1371, and ref. cited therein.

[25] R. B. Gupta, R. W. Franck, *J. Am. Chem. Soc.* **109** (1987) 5393. – For the isolation of a zwitterion in a [4 + 2] cycloaddition see: K. P. Hartmann, M. Heuschmann, *Angew. Chem.* **101** (1989) 1288; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 1267.

[26] For Diels-Alder reactions with normal electron demand see: J. Sauer, D. Lang, W. Wiest, *Chem. Ber.* **97** (1964) 3208.

[27] For Diels-Alder reactions with inverse electron demand see: ref.[12,14d]; H. Meier, H.-L. Eckes, H.-P. Niedermann, H. Kolshorn, *Angew. Chem.* **99** (1987) 1040; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 1046.

[28] For 1,3-dipolar cycloadditions see: R. Huisgen, *Angew. Chem.* **75** (1963) 742 and in *1,3-Dipolar Cycloaddition Chemistry* (A. Padwa, Ed.), vol. 1, p. 126, John Wiley & Sons, New York, 1984.

[29] For the 1,3-dipolar cycloaddition of mesityl nitrile oxide to **1b/1d** a $k_{E/Z}$ value of approximately 3 was determined; the $Cu(acac)_2$-catalyzed reaction of methyl diazoacetate towards **1b/1d** favoured the *Z* isomer ($k_{E/Z} \approx 0.3$): Nils Basso, *Diplomarbeit*, Technische Hochschule Darmstadt, 1989. The higher reactivity of *Z* enol ethers towards ketenes is well-known (H. Mayr, R. Huisgen, *Tetrahedron Lett.* **1975**, 2965) and was confirmed in experiments employing **1b/1d** ($k_{Z/E} > 25$), see ref.[18].

[30] For the cycloaddition of bis(siloxy)ethenes **1f/1e** with a tetrazine derivative a $k_{E/Z}$ of 10 was determined; B. Tischler, *Diplomarbeit*, University of Regensburg, 1985.

[31] See K. N. Houk, *Top. Curr. Chem.* **79** (1979) 1, and ref. cited therein.

[32] PM3 calculations of the transition states of the cycloaddition of a nitroso alkene with *E/Z*-isomeric silyl enol ethers also reveal no large difference in energy (R. Sustmann, private communication).

[33] R. Huisgen, G. Steiner, *Tetrahedron Lett.* **1973**, 3763. – See also: R. Brückner, R. Huisgen, *Tetrahedron Lett.* **31** (1990) 2557.

[34] However, the more reactive nitroso alkene **2d** provides cycloadducts with these olefins, although in low yields (R. Zimmer, H.-U. Reißig, unpublished results).

[35] R. Zimmer, H.-U. Reißig, *Angew. Chem.* **100** (1988) 1576, *Angew. Chem. Int. Ed. Engl.* **27** (1988) 1518. – R. Zimmer, H.-U. Reißig, *Synthesis* **1989**, 908.

[36] H. Henneberger, *Dissertation*, University of Würzburg, 1987.

[37] R. Huisgen, P. H. J. Ooms, M. Mingin, N. L. Allinger, *J. Am. Chem. Soc.* **102** (1980) 3951. – Also see: M. Christl, B. Mattauch, H. Irngartinger, A. Goldmann, *Chem. Ber.* **119** (1986) 950 and M. Christl, E. Brunn, W. R. Roth, H.-W. Lennartz, *Tetrahedron* **45** (1989) 2905.

[38] M. H. Novice, H. R. Seikaly, A. D. Seiz, T. T. Tidwell, *J. Am. Chem. Soc.* **102** (1980) 5835, and ref. cited therein.

[39] J. Bartl, S. Steenken, H. Mayr, 9th IUPAC Conference on Physical Organic Chemistry, Regensburg 1988, Abstract P 83.

[40] R. Huisgen in *Methoden der Organischen Chemie* (Houben-Weyl), 4th ed., vol. III/1, p. 143, Thieme-Verlag, Stuttgart, 1955.

[178/90]