207. 1,3-Dipolar Cycloadditions to Strained Olefins[1])

by **Konrad B. Becker** and **Martin K. Hohermuth**

Institut für Organische Chemie der Universität Basel, St. Johanns-Ring 19, CH-4056 Basel

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Summary

The *Bredt* olefins bicyclo[3.3.1]non-1-ene (**2**), bicyclo[4.2.1]non-1(8)-ene (**3**), and bicyclo[4.2.1]non-1(2)-ene (**4**) react rapidly with 1,3-dipoles such as diazomethane, phenyl azide, and mesitonitrile oxide to yield mixtures of two regioisomeric cycloadducts **10**, **11** and **12**, respectively. On the contrary, cycloaddition to the comparable monocyclic 1-methyl-(*E*)-cyclooctene (**5**) is fairly regioselective. 2-Methylnorborn-2-ene (**6**) gives one isomer with mesitonitrile oxide (as do less strained olefins), but mixtures with diazomethane and phenyl azide. ^{1}H-NMR. and ^{13}C-NMR. spectra of the cycloadducts are reported. The results are discussed in the light of frontier molecular orbital theory.

Introduction. – 1,3-Dipolar cycloadditions to olefins have been extensively studied and are now well understood primarily owing to the efforts of *Huisgen* [1]. Experience indicates a concerted mechanism [2], and frontier molecular orbital theory has explained successfully relative rates and the regioselectivity of these cycloadditions [3]. A two-step diradical mechanism is advocated by *Firestone* [4], but this theory stands on weaker grounds [5].

Alkyl-substituted olefins and particularly trisubstituted olefins show low reactivity against the common 1,3-dipolar reagents [1] and therefore have been studied only rarely [6]. However, introduction of strain makes such compounds good candidates for 1,3-dipolar cycloadditions. *Alder & Stein* [7] used phenyl azide to detect and characterize the strained double bond in bicyclo[2.2.1]hept-2-enes (norbornenes). (*E*)-Cyclooctene (**1**) [8], cyclopropenes and methylenecyclopropane [9] react with a number of 1,3-dipolar reagents that are inert against normal cycloolefins. *Wiseman & Pletcher* [10] reported that the strained *Bredt* olefin bicyclo[3.3.1]non-1-ene (**2**) combines with diazomethane.

With a good synthesis of the methylene-bridged (*E*)-cyclooctenes bicyclo[3.3.1]-non-1-ene (**2**), bicyclo[4.2.1]non-1(8)-ene (**3**) and bicyclo[4.2.1]non-1-ene (**4**) at hand [11], cycloadditions of 1,3-dipoles to these *Bredt* olefins can now be examined in detail. In order to separate the influence of strain and of alkyl substituents in general on the regioselectivity of the cycloaddition, a number of other trisubstituted

[1]) Taken in part from the planned dissertation of M.K.H.

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olefins were included in this study. The choice of the 1,3-dipoles diazomethane, phenyl azide, and mesitonitrile oxide[2]) should allow testing the applicability of frontier molecular orbital theory or diradical theory to the cycloaddition. The influence of steric hindrance may be evaluated by comparison of phenyl azide and mesitonitrile oxide additions.

Results. – *Addition of diazomethane.* The *Bredt* olefins **2**, **3**, **4**, and the comparable monocyclic 1-methyl-(*E*)-cyclooctene (**5**)[3]) react with excess diazomethane in ether at 4° within a few days. The addition to 2-methylnorborn-2-ene (**6**) is very sluggish. After three weeks, only a few percent of the cycloadduct **14** are observed. 1-Methylcyclopentene (**7**) and 2-methylbut-2-ene (**8**) are inert towards diazomethane.

The adducts **10**–**14** were separated from polymeric material by flash distillation in a bulb tube and analyzed by NMR. spectroscopy. In all cases, a mixture of two isomers is observed. Whereas the olefins **2**, **3** and **4** predominantly yield the regioisomer with the diazomethane C-atom bound to the fully substituted C-atom, *i.e.* **10a**[4]), **11a** and **12a**, isomers **13b** and **14b** are the main products obtained from 1-methyl-(*E*)-cyclooctene (**5**) and 2-methylnorborn-2-ene (**6**), respectively *(Table 1)*.

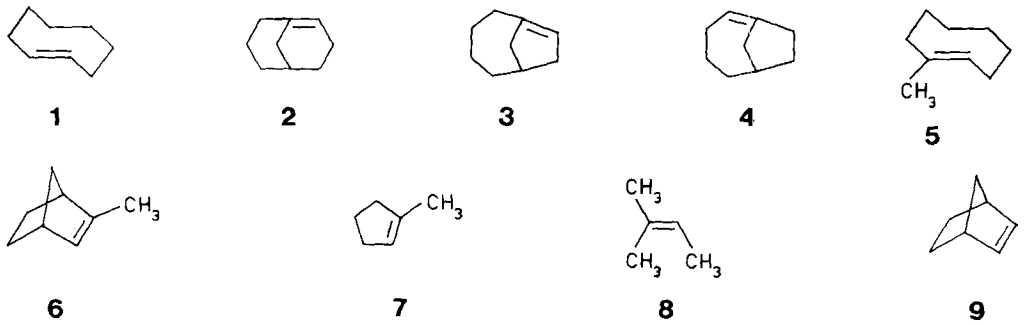
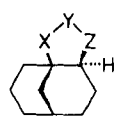


Table 1. *Products obtained on addition of 1,3-dipoles to trisubstituted olefins*[a]).

Olefin	CH_2N_2	$C_6H_5N_3$	$(CH_3)_3C_6H_2CNO$
2	**10a**:**10b** = 70:30	**10c**:**10d** = 33:67	**10e**:**10f** = 90:10
3	**11a**:**11b** = 67:33	**11c**:**11d** = 45:55	**11e**:**11f** = 77:23
4	**12a**:**12b** = 60:40	**12c**:**12d** = 33:67	**12e**:**12f** = 64:36
5	**13a**:**13b** = 7:93	**13c**	**13e**
6	**14b**, > 80%	**14c**:**14d** = 75:25	**14e**
7	[b])	**15c**	**15e**
8	[b])	[b])	**16e**

[a]) Product composition determined by NMR. spectroscopy on crude reaction products, ± 5%.
[b]) No product formation.

[2]) 2,4,6-Trimethylbenzonitrile oxide.
[3]) We thank Prof. *Whitham* for a detailed procedure for the synthesis of **5** [12].
[4]) *Wiseman & Pletcher* [10] report an adduct of diazomethane with **2** in 99% yield, to which they ascribe structure **10b**. Their spectral data, however, are those of isomer **10a**.



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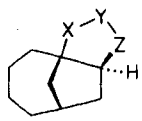

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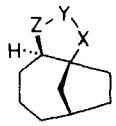

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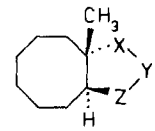

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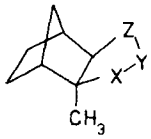

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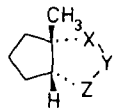

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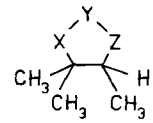

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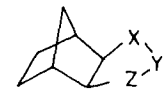

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a –X–Y–Z–=–CH_2–N=N–

b –X–Y–Z–=–N=N–CH_2–

c –X–Y–Z–=–N(–C_6H_5)–N=N–

d –X–Y–Z–=–N=N–N(–C_6H_5)–

e –X–Y–Z–=–O–N=C(–$C_6H_2(CH_3)_3$)–

f –X–Y–Z–=–C=N–O–(–$C_6H_2(CH_3)_3$)

^{1}H-NMR. spectroscopy *(Table 2)* allows unambiguous distinction of regioisomers **a** and **b** and the determination of their relative amounts in the crude product. The protons of the original methylene C-atom of diazomethane give rise to an *AB*-quartet at δ 3.7–4.9 ppm with a geminal coupling constant $J = ca.$ 18 Hz. In isomer **a**, this quartet is split further by a small coupling constant (1.5–3.5 Hz) as the result of five-bond coupling over the N=N-bridge [14] to a methine proton at $\delta = ca.$ 4 ppm, the original vinyl proton. In isomer **b**, the *AB*-quartet couples to a proton at $\delta = ca.$ 2 ppm with $J = 5$–9 Hz as expected for a vicinal coupling constant. The size of the coupling constants is in accord with the configuration depicted in **10**–**14**, but, owing to the uncertainty about the preferred conformation of the cycloadducts, the correct configuration is hard to prove.

The ^{13}C-NMR. spectra confirm the structures of the regioisomers **a** and **b** and their relative amounts in the crude product *(Table 3)*. The two C-atoms α to the N=N double bond are readily assigned by their chemical shift. Off-resonance proton-decoupled spectra allow the distinction of the methylene C-atom derived from the original diazomethane and the methine or fully substituted C-atom in isomer **a** and **b**, respectively. For comparison, the spectral data of the cycloadduct **17a**, **b** [15] obtained from norbornene (**9**) are included in *Tables 2* and *3*.

Addition of phenyl azide. The reaction of the olefins **2**, **3** and **4** with a slight excess of phenyl azide in pentane gives a mixture of two cycloadducts **10**–**12** in a few hours at RT. *(Table 1)*. Under the same conditions, 1-methyl-(*E*)-cyclooctene (**5**) yields a single product identified as **13c**[5]). A mixture of regioisomers **14c** and **14d** is formed from 2-methylnorborn-2-ene (**6**) after three days at RT. Complete addition of phenyl azide to 1-methylcyclopentene (**7**) requires 40 days at 45°. At higher temperatures, cycloadduct **15c** decomposes to a considerable extent. No clean adduct **16** was obtained from 2-methylbut-2-ene (**8**).

[5]) *Bridges & Whitham* tentatively assigned structure **13d** to the addition product of **5** with phenyl azide [13].

Table 2. *Selected ^1H-NMR. values for adducts* **10–17**[a])

	a						**b**					**c**		**d**		**e**		**f**	
	δH_A	δH_B	δH_C	J_{AB}	J_{AC}	J_{BC}	δH_A	δH_B	J_{AB}	J_{AX}	J_{BX}	δ	J	δ	J	δ	J	δ	J
10	4.32	3.95	4.0	18	3.5	2	4.80	4.05	18	9	6	3.92	10, 7	3.56	11, 5	3.27	10.5, 7.5	4.41	7, 6
11	4.68	3.90	4.45	17.5	2.5	2	4.80	4.15	18.5	10	5	4.71	10, 8	3.82	8, 6	3.60	10, 6	4.91	8, 4
12	4.63	4.18	3.7	18	2.5	3	4.86	3.75	18	9.5	9.5	3.92	12, 6	3.17	14, 5	3.41	10, 6	4.31	10, 6
13			[b])				4.81	3.73	17	11	8	3.92	10, 4	[b])		3.39	8, 6	[b])	
14		*ca.* 3.7			[c])		4.62	4.06	18.5	9	3.5	4.02	< 1	3.20	< 1	2.67	1.5	[b])	
15			[b])						[b])			4.62	5, 5	[b])		3.42	7, 4	[b])	
16			[b])						[b])			[b])		[b])		3.22	7.5	[b])	
17[d])	4.5	4.05	4.6	18	1.5	3.5	4.5	4.05	18	9	4	4.41	9, < 1	3.54	9, < 1	3.10	8, < 1	4.42	8, < 1

[a]) In $CDCl_3$, δ in ppm, J in Hz. [b]) Not observed. [c]) Not resolved. [d]) **17a = 17b, 17c = 17d, 17e = 17f.**

Table 3. *Selected ^{13}C-NMR. values for adducts* **10–17**[a])

	a			**b**			**c**		**d**		**e**		**f**	
	δC	δCH_2	δCH	δC	δCH_2	δCH	δC	δCH	δC	δCH	δC	δCH	δC	δCH
10	35.0	89.4	89.9	90.4	83.3	[c])	[b])		[b])		[b])		[b])	
11	47.3	89.6	100.7	106.0	85.4	43.2	69.8	93.8	94.3	66.8	96.9	61.8	68.1	97.6
13	39.3	91.9	91.0	88.3	82.5	40.1	69.8	83.4	[b])		88.9	56.6	[b])	
14		[c])		100.0	84.0	43.2	66.9	93.4	89.0	66.5	92.9	66.6	[b])	
15		[b])			[b])		67.8	91.2	[b])		94.9	61.4	[b])	
16		[b])			[b])		[b])		[b])		85.7	53.7	[b])	
17[d])	–	–	96.7	–	82.8	37.8	–	86.1	–	60.1	–	61.3	–	86.7

[a]) In $CDCl_3$, δ in ppm (TMS $\delta = 0$). [b]) Not observed. [c]) Not resolved. [d]) **17a = 17b, 17c = 17d, 17e = 17f.**

The ^{1}H-NMR. spectra allow unambiguous assignment of structure **c** or **d** to the adducts *(Table 2)*. In isomer **c**, the original vinylic proton is now α to a N=N double bond and resonates within ± 0.3 ppm of the corresponding absorption in the comparable diazomethane cycloadduct **a**. The proton α to the single bonded N-atom in isomer **d** absorbs at consistently higher field, and the chemical shift difference is comparable to that found between the protons in the phenyl azide cycloadducts **17c**, **d** [16] of norbornene (**9**). The coupling constants are in accord with the configuration shown. The ^{13}C-NMR. spectra confirm the assignment of isomer **c** and **d**. A chemical shift difference of more than 22 ppm is found for C-atoms α to single or double bonded N-atoms *(Table 3)*.

Addition of mesitonitrile oxide. The olefins **2**, **3** and **4**, and 1-methyl-(*E*)-cyclooctene (**5**) react with mesitonitrile oxide in pentane in a few minutes at RT. The formation of a mesitonitrile oxide cycloadduct is also observed with 2-methylnorborn-2-ene (**6**), 1-methylcyclopentene (**7**), and 2-methylbut-2-ene (**8**) on prolonged reaction time. Whereas **2**, **3** and **4** give a mixture of two regioisomers **10–12 e** and **f**, only isomers **13–16 e** are formed from **5–8** *(Table 1)*.

Identification of isomers **e** and **f** is straightforward by the ^{1}H-NMR. spectra. The proton α to the O-atom in isomer **e** absorbs at δ 4.3–4.9 ppm, whereas the proton α to the C=N double bond in isomer **f** appears at δ 2.7–3.6 ppm. A difference of more than 26 ppm for the corresponding C-atoms is found in the ^{13}C-NMR. spectra *(Table 3)*. Similar shift differences are observed in the norbornene cycloadduct **17e, f**.

Discussion. – The *Bredt* olefins **2**, **3** and **4** react with diazomethane, phenyl azide, and mesitonitrile oxide to give mixtures of two regioisomers. Similarly, 2-methylnorborn-2-ene (**6**) yields mixtures with diazomethane and phenyl azide, but one isomer only with mesitonitrile oxide. The addition of these three dipoles to 1-methyl-(*E*)-cyclooctene (**5**) is fairly regioselective, as is the addition of phenyl azide or mesitonitrile oxide to 1-methylcyclopentene (**7**) and of mesitonitrile oxide to 2-methylbut-2-ene (**8**). A profound influence of double bond strain on the reactivity towards 1,3-dipolar reagents is noted[6]).

A careful search for other products did not substantiate the formation of stereoisomers. This is in line with previous experience with 1,3-dipolar cycloadditions and is a prerequisite for a concerted reaction mechanism [2]. A diradical intermediate cannot be rigorously excluded. However, one would have to accept that these diradicals isomerize considerably more slowly than they revert to starting material or collapse to products [4].

Frontier molecular orbital theory has been applied with success to the problem of regioselectivity and reactivity in 1,3-dipolar cycloadditions [3]. This approach should also explain the regiochemistry found with the addition of 1,3-dipoles to trialkyl-substituted olefins. According to this theory, bond formation is dictated primarily by the overlap of the $HOMO_{dipole}$-$LUMO_{olefin}$ and the $LUMO_{dipole}$-$HOMO_{olefin}$ with the appropriate symmetry. Which of these interactions will

[6]) The reaction rate constants for the addition of phenyl azide to the olefins **2–5** have been determined; they will be discussed elsewhere in connection with strain energies estimated from hydrogenation enthalpies and calculated with force field methods [17].

Table 4. *Approximate HOMO and LUMO energies* (eV) *of 1,3-dipoles and alkyl-substituted olefins* [3b]

	CH_2N_2	$C_6H_5N_3$	$(CH_3)_3C_6H_2CNO$[a])	$R_2C{=}CHR$	**2, 3, 4**[b])
LUMO	+1.8[c])	−0.2	+ 0.1	+2.5	+2
HOMO	−9	−9.5	−10.3	−8.5	−8.5

[a]) Data for mesitonitrile oxide from [19]. [b]) See discussion in the text.
[c]) Next lowest unoccupied molecular orbital. The LUMO (+0.2 eV) lies in the plane and does not combine with the $HOMO_{olefin}$.

dominate is determined by the relative energy differences of either pair of orbitals. The regioselectivity is then the result of best orbital overlap, *i.e.* the atoms with the largest orbital coefficients combine preferentially. The energy of the HOMO may be derived approximately from the vertical ionization potential (IP_V) using *Koopmans* theorem. These ionization potentials have been measured for (*E*)-cyclooctene (**1**) and the bicyclo[4.2.1]nonenes **3** and **4** [18] and shown to lie within the range of ionization potentials of unstrained olefins with similar substitution pattern. The energy of the LUMO is related to the electron affinity, but for most dipoles and olefins, these data are not available. Relative LUMO energies may be obtained from reduction potentials, charge transfer energies, or UV. spectra [3b]. The UV. spectra of **2**, **3** and **4** [11] suggest that the LUMO energies of these strained olefins are similar or at most 0.5 eV lower than the LUMO energies of unstrained trialkyl-substituted olefins. Some of the HOMO and LUMO energies pertinent to the discussion are collected in *Table 4*.

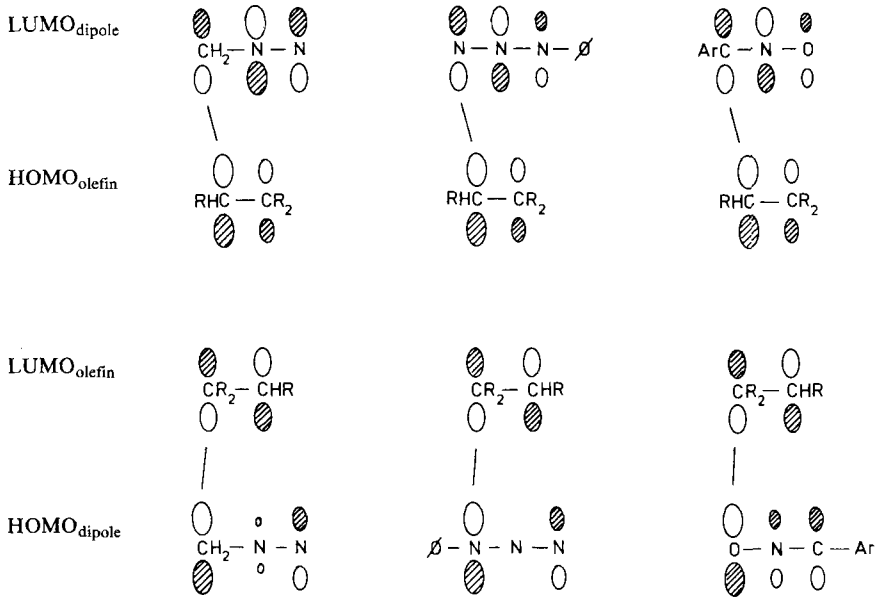
Calculation of the HOMO-LUMO energy differences from the data in *Table 4* leads to the conclusion that the cycloaddition of phenyl azide and mesitonitrile oxide to trialkyl-substituted olefins is controlled by the $LUMO_{dipole}$-$HOMO_{olefin}$ interaction, whereas both HOMO-LUMO interactions must be considered for additions of diazomethane[7]).

The orbital coefficients of the HOMO and LUMO of the dipoles and the olefin are presented in generalized form by the size of the orbital lobes in the *Scheme*. The orbital coefficients of trialkyl-substituted olefins are comparable to those of propene [20], because an additional alkyl substituent at either end of the double bond should not substantially alter the relative size of the coefficients. Hence, the larger coefficient is found at the less substituted C-atom in the HOMO and at the more substituted C-atom in the LUMO. In the LUMO, the difference between the orbital coefficients is small and may even be reversed on interaction with a nucleophilic partner, as has been calculated for a complex of propene and hydride ion [20].

$LUMO_{dipole}$-$HOMO_{olefin}$ interaction leads to regioisomers **b**, **c** and **e** by combination of the 'more electrophilic' dipole end (larger LUMO coefficient, *i.e.* the C-atom in diazomethane, the unsubstituted N-atom in phenyl azide, and the C-atom in mesitonitrile oxide [3b]) with the less substituted olefinic C-atom. In diazomethane, the LUMO coefficient at the C-atom is only slightly larger than at the N-atom. Therefore, isomer **a** should also be formed. $LUMO_{olefin}$-$HOMO_{dipole}$

[7]) This is consistent with the general classification of 1,3-dipoles according to *Sustmann* [3c].

Scheme. *Generalized representation of orbital coefficients and orbital overlap*[a])



[a]) Orbital coefficients derived from [3b] [20].

interaction gives mixtures, in which isomers **a**, **c** and **e** predominate. However, this interaction plays a role in additions of diazomethane only *(vide supra)*.

Frontier molecular orbital theory correctly predicts the isomers formed from 2-methylbut-2-ene (**8**), 1-methylcyclopentene (**7**), and 1-methyl-(*E*)-cyclooctene (**5**), and the mixtures obtained from cycloadditions of diazomethane. However, appreciable amounts of the 'wrong' isomer **d** and **f** are found in cycloadditions of phenyl azide and mesitonitrile oxide, respectively, to **2**, **3** and **4**. Unexpectedly, 2-methylnorborn-2-ene (**6**) yields a mixture of **14c** and **14d** from phenyl azide.

Steric hindrance cannot be the reason for the exceptional behaviour of bridgehead olefins **2**, **3** and **4**. On the contrary, molecular models suggest that steric interactions between these compounds and 1,3-dipoles are reduced and the double bond is more accessible than in comparable olefins. In the case of the fairly rigid 2-methylnorborn-2-ene (**6**), the methyl group in combination with the methylene bridge (C(7)) may hinder the formation of regioisomer **c** (and **f**) and lead to an increased amount of isomer **d** (and **e**).

The difference observed between prediction and experiment must primarily be the result of the *strain in the double bond* [21]. 2-Methylnorborn-2-ene (**6**) and to a lesser extent 1-methylcyclopentene (**7**) display in-plane deformation of the bond to the alkyl (ring) substituents. The strain in olefins **2**–**5** leeds to twist and out-of-plane deformation of the double bond. In 1-methyl-(*E*)-cyclooctene (**5**), twist deformation is dominant [22], whereas in **2**, **3** and **4**, the out-of-plane deformation at the bridgehead prevails [23]. This out-of-plane deformation will alter the

mixing of alkyl substituent orbitals with the localized π-bond orbital. Hence, the extrapolation of orbital coefficients from propene to strained bridgehead olefins is useless. As a further consequence of the twist and out-of-plane deformation of the double bond, secondary orbital interactions, *e.g.* with in-plane orbitals of the 1,3-dipoles, may become increasingly important.

The HOMO and LUMO energies for compounds **2**–**5** are similar to those of comparable unstrained olefins *(Table 4)*. Therefore, the usual correlation found between HOMO-LUMO energy differences and reaction rate constants [3c] breaks down in the case of strained olefins. The rehybridization as a consequence of double bond distortion will increase the orbital overlap with the dipole and therefore be responsible for the increased reactivity of strained olefins [8a].

Although diradical intermediates probably are not formed during cycloadditions of 1,3-dipoles [5], we shall examine our results in the light of this theory [4]. The regiochemistry of the addition of mesitonitrile oxide to olefins **5**–**8** is predicted correctly. Additional assumptions about dipole-dipole interactions in the transition state are necessary to account for the formation of isomer **c** from trialkyl-substituted olefins and phenyl azide. However, diazomethane should give isomer **b** as the only cycloadduct. The product mixtures obtained from **2**, **3** and **4** can only be rationalized if one assumes that the secondary carbon radical is comparable in stability with the bridgehead tertiary radical. The latter might be destabilized, because it cannot adopt the usual planar conformation. This assumption, however, is unreasonable in the light of the experimental observation that on protonation, **2**, **3** and **4** still form the bridgehead carbenium ion exclusively [24].

In summary, frontier orbital theory nicely predicts and explains the regioisomers formed from unstrained trialkyl-substituted olefins. It is not surprising that this simple method in its original form cannot handle torsionally strained bridgehead olefins. These show enhanced reactivity and yield mixtures of regioisomers as a consequence of rehybridization of the double bond.

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Experimental Part

General remarks. Melting points (m.p.) are corrected, boiling points (b.p.) are not corrected. IR. spectra (cm^{-1}) were recorded on a *Perkin-Elmer* 125. ^{1}H-NMR. spectra at 90 MHz and ^{13}C-NMR. spectra at 22.63 MHz (δ ppm/TMS, J Hz) were measured on a *Bruker* WH-90 *Fourier* transform spectrometer by Mr. *K. Aegerter*. The multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, qa = quartet, m = multiplet. Mass spectra were recorded on a *AEI*-MS 30 at 70 eV. UV. spectra (λ_{max} nm ($\log\varepsilon$)) were measured on a *Beckman* DK 2. Elemental analyses were carried out by Mr. *E. Thommen*. Abbreviations: RT. = room temperature, HV. = high vacuum, GC. = gas chromatography.

Olefins. Bicyclo[3.3.1]non-1-ene (**2**), bicyclo[4.2.1]non-1(8)-ene (**3**), and bicyclo[4.2.1]non-1-ene (**4**) were freshly prepared by intramolecular *Wittig* reaction [11]. 1-Methyl-(*E*)-cyclooctene (**5**) was obtained according to *Bridges & Whitham* [12]. *Exo*-2-methylnorbornan-2-ol was dehydrated with phosphorous oxychloride in pyridine [25] to give a 3:2 mixture of 2-methylidenenorbornane and 2-methylnorborn-2-ene (**6**). Pure **6** was obtained by fractional distillation and prep. GC. (SE 52, 70°). 1-Methylcyclopentene (**7**), 2-methylbut-2-ene (**8**) and norbornene (**9**) were commercial products. Their purity was checked by NMR. and GC.

Pyrazolines from strained olefins and diazomethane. – The olefins were mixed with a tenfold excess of diazomethane in ether (prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) and kept at 4° under N_2 for 5 to 10 days. The solution was evaporated i.V. at 0° and the product isolated by flash distillation in a bulb tube at reduced pressure. – ^{1}H-NMR. (90 MHz, $CDCl_3$): see *Table 2.*

3,4-Diazatricyclo[6.3.1.0^{1,5}]dodec-3-ene (**10a**) *and 2,3-diazatricyclo[6.3.1.0^{1,5}]dodec-2-ene* (**10b**). From bicyclo[3.3.1]non-1-ene (**2**), 71% of **10a** and **10b** (70:30), very hygroscopic crystals, m.p. 70–74° (dec.) ([10] m.p. 83–85°). – ^{13}C-NMR. ($CDCl_3$) **10a**: 89.9 (*d*, C(5)), 89.4 (*t*, C(2)), 35.8, 35.0 (*s*, C(1)), 34.3, 31.4, 26.4 (*d*, C(8)), 24.9, 22.6, 19.9. **10b**: 90.4 (*s*, C(1)), 83.3 (*t*, C(4)), 34.8, 34.7, 31.7, 31.2, 26.1, 25.5, 25.2, 18.0.

$C_{10}H_{16}N_2$ (164.24) Calc. C 73.12 H 9.82 N 17.06% Found C 72.83 H 9.90 N 16.88%

3,4-Diazatricyclo[5.4.1.0^{1,5}]dodec-3-ene (**11a**) *and 2,3-diazatricyclo[5.4.1.0^{1,5}]dodec-2-ene* (**11b**). From bicyclo[4.2.1]non-1(8)-ene (**3**), 70% of **11a** and **11b** (67:33), very hygroscopic crystals, m.p. 23–26°. – UV. (EtOH): 322 (2.5). – IR. (CCl_4): 2920, 2855, 1540 (N=N), 1450, 1105, 925, 900. – ^{13}C-NMR. ($CDCl_3$) **11a**: 100.7 (*d*, C(5)), 89.6 (*t*, C(2)), 47.3 (*s*, C(1)), 40.7, 37.5 (*d*, C(7)), 36.2, 35.9, 35.1, 26.4, 23.8. **11b**: 106.0 (*s*, C(1)), 85.4 (*t*, C(4)), 43.2 (*d*, C(5) or C(7)), 40.2, 39.5, 38.7, 35.4, 35.2, 25.3, 24.5.

$C_{10}H_{16}N_2$ (164.24) Calc. C 73.12 H 9.82 N 17.06% Found C 72.86 H 9.94 N 17.12%

3,4-Diazatricyclo[7.2.1.0^{1,5}]dodec-3-ene (**12a**) *and 2,3-diazatricyclo[7.2.1.0^{1,5}]dodec-2-ene* (**12b**). From bicyclo[4.2.1]non-1-ene (**4**) as a mixture of **12a** and **12b** (60:40), very hygroscopic syrup. Owing to the instability of the compound and the small amount produced, only the ^{1}H-NMR. spectrum was recorded *(Table 2).*

1-Methyl-9,10-diaza-trans-*bicyclo[6.3.0]undec-9-ene* (**13a**) *and 8-methyl-9,10-diaza*-trans-*bicyclo-[6.3.0]undec-9-ene* (**13b**). From 1-methyl-(*E*)-cyclooctene (**5**), 79% of **13a** and **13b** (7:93), very hygroscopic liquid [13]. – IR. (film): 2920, 2850, 1550 (N=N), 1460, 1445, 1369, 1205, 1125, 1115, 905, 895. – ^{1}H-NMR. ($CDCl_3$): 0.97 (*s*, CH_3 **13b**), 0.77 (*s*, CH_3 **13a**). Other signals see *Table 2.* – ^{13}C-NMR. ($CDCl_3$) **13b**: 88.3 (*s*, C(8)), 82.5 (*t*, C(11)), 40.6, 40.1 (*d*, C(1)), 29.3, 27.9, 27.4, 26.4, 23.7, 15.9 (*qa*, CH_3). **13a**: 91.9 (*t*, C(11)), 91.0 (*d*, C(8)), 39.3 (*s*, C(1)). Other signals only partially resolved.

$C_{11}H_{18}N_2$ (166.26) Calc. C 72.24 H 10.91 N 16.85% Found C 71.63 H 11.15 N 16.37%

6-Methyl-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-ene (**14a**) *and 2-methyl-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-ene* (**14b**). From 2-methylnorbornene (**6**), 10% of a mixture containing > 80% **14b** after 3 weeks, very hygroscopic liquid, unstable at RT. **14a** could not be identified with certainty. – IR. ($CDCl_3$): 2960, 2930, 2880, 1600, 1550, 1445, 1375, 1347, 1130, 1105, 1055. – ^{13}C-NMR. (CD_2Cl_2, –60°) **14b**: 100.0 (*s*, C(2)), 84.0 (*t*, C(5)), 44.4, 43.3, 43.2 (each *d*, C(1), C(6), C(7)), 33.9, 28.0, 23.4 (each *t*, C(8), C(9), C(10)), 19.1 (*qa*, CH_3).

3,4-Diazatricyclo[5.2.1.0^{2,6}]dec-3-ene (**17a, b**). 80% from norbornene (**9**) as a very hygroscopic liquid [15]. – ^{13}C-NMR. ($CDCl_3$): 96.7 (*d*, C(2)), 82.8 (*t*, C(5)), 41.2, 39.1, 37.8 (each *d*, C(1), C(6), C(7)), 31.3, 28.1, 26.2 (each *t*, C(8), C(9), C(10)).

$C_8H_{12}N_2$ (136.19) Calc. C 70.55 H 8.88 N 20.57% Found C 70.32 H 9.00 N 20.75%

Phenyltriazolines from strained olefins and phenyl azide. – The olefins were dissolved in a solution of 1.05 mol-equiv. of phenyl azide in pentane and kept at RT. for 5 days under N_2. The crude product obtained on evaporation i.V. was analyzed by NMR. Pure isomers were obtained by fractional crystallization from pentane or petroleum ether. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 6.9–8.6 (*m*, 5 H, C_6H_5). Other signals see *Table 2.*

2-Phenyl-2,3,4-triazatricyclo[6.3.1.0^{1,5}]dodec-3-ene (**10c**) *and 4-phenyl-2,3,4-triazatricyclo-[6.3.1.0^{1,5}]dodec-2-ene* (**10d**). From bicyclo[3.3.1]non-1-ene (**2**) as a mixture of **10c** and **10d** (33:67). (From petroleum ether pure **10d**, m.p. 104.5–105.5°). – IR. (CCl_4): 2967, 2932, 1595, 1490, 1350, 1112, 920, 685.

$C_{15}H_{19}N_3$ (241.34) Calc. C 74.65 H 7.94 N 17.41% Found C 74.45 H 8.05 N 17.32%

2-Phenyl-2,3,4-triazatricyclo[5.4.1.0^{1,5}]dodec-3-ene (**11c**) *and 4-phenyl-2,3,4-triazatricyclo-[5.4.1.0^{1,5}]dodec-2-ene* (**11d**). From bicyclo[4.2.1]non-1(8)-ene (**3**) as a mixture of isomers **11c** and **11d** (45:55), separated by fractional crystallization. **11c**: m.p. 99–106° (dec.). – UV. (pentane): 283

(4.05), 233 (3.85), 212 (4.03). – IR. (CCl_4): 2930, 2810, 1600, 1490, 1340, 1110, 1095, 1035, 1010, 685. – ^{13}C-NMR. ($CDCl_3$): 139.7, 129.1, 122.4, 116.1, 93.8 (*d*, C(5)), 69.8 (*s*, C(1)), 42.4, 37.7, 36.4 (*d*, C(7)), 35.3, 34.5, 24.9, 24.2. – MS.: No M^+, 213 ($M^+ - N_2$), 77 (100%).

$C_{15}H_{19}N_3$ (241.34) Calc. C 74.65 H 7.94 N 17.41% Found C 74.47 H 8.00 N 17.30%

11d: m.p. 81–90° (dec.). – UV. (pentane): 283 (3.99), 216 (4.17). – IR. (CCl_4): 2930, 2860, 1600, 1500, 1487, 1452, 1353, 1110, 1082, 1033, 1004, 980, 685. – ^{13}C-NMR. ($CDCl_3$): 140.6, 129.3, 121.9, 113.9, 94.3 (*s*, C(1)), 66.8 (*d*, C(5)), 41.4, 40.4, 37.1 (*d*, C(7)), 36.0, 35.4, 24.9, 24.5. – MS.: No M^+, 213 ($M^+ - N_2$), 170 (100%).

$C_{15}H_{19}N_3$ (241.34) Calc. C 74.65 H 7.94 N 17.41% Found C 74.52 H 8.10 N 17.48%

2-Phenyl-2,3,4-triazatricyclo[7.2.1.0^{1,5}]dodec-3-ene (**12c**) *and 4-phenyl-2,3,4-triazatricyclo[7.2.1.0^{1,5}]-dodec-2-ene* (**12d**). From bicyclo[4.2.1]non-1-ene (**4**) as a mixture of **12c** and **12d** (33:67). – **12d**: m.p. 108.5–111° (dec.). – UV. (pentane): 281 (4.03), 238 (3.78). – IR. (CCl_4): 2978, 2960, 2930, 1590, 1480, 1345, 1087, 685.

$C_{15}H_{19}N_3$ (241.34) Calc. C 74.65 H 7.94 N 17.41% Found C 74.78 H 8.16 N 17.42%

1-Methyl-11-phenyl-9,10,11-triaza-trans-*bicyclo[6.3.0]undec-9-ene* (**13c**). From 1-methyl-(*E*)-cyclooctene (**5**), 93% of **13c**, m.p. 80–94° (dec.) ([13] m.p. 81°). – UV. (pentane): 275 (3.89), 242 (4.08), 215 (3.95). – IR. (KBr): 2920, 1600, 1485, 1455, 1368, 1275, 755, 700, 695. – ^{1}H-NMR. ($CDCl_3$): 0.80 (*s*, CH_3). Other signals see *Table 2*. – ^{13}C-NMR. ($CDCl_3$): 140.4, 128.7, 125.9, 124.1, 83.4 (*d*, C(8)), 69.8 (*s*, C(1)), 40.7, 28.5, 27.9, 27.2 (2 C), 24.2, 15.9 (*qa*, CH_3).

6-Methyl-5-phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (**14c**) *and 2-methyl-5-phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene* (**14d**). From 2-methylnorborn-2-ene (**6**) as a mixture of **14c** and **14d** (75:25), oily liquid ([26] m.p. 98° after crystallization from petroleum ether). – IR. (film): 2970, 2930, 2875, 1600, 1490, 1450, 1338, 1140, 1095, 1045, 745, 687. – ^{13}C-NMR. ($CDCl_3$). **14c**: 139.7, 129.2, 120.8, 115.6, 93.4 (*d*, C(2)), 66.9 (*s*, C(6)), 45.0 and 43.2 (each *d*, C(1) and C(7)), 34.6 (*t*, C(10)), 25.6 and 24.0 (each *t*, C(8) and C(9)), 21.3 (*qa*, CH_3). **14d**: 89.0 (*s*, C(2)), 66.5 (*d*, C(6)), 42.0, 37.3 (each *d*, C(1) and C(7)), other absorptions only partially resolved.

5-Methyl-4-phenyl-2,3,4-triazabicyclo[3.3.0]oct-2-ene (**15c**). From 1-methylcyclopentene (**7**) and 1.05 equivalents of phenyl azide in pentane at 45° for 40 days (sealed Pyrex pressure tube). M.p. 204–205° (petroleum ether). Decomposition was noted on further recrystallization. – IR. (CCl_4): 2960, 2930, 2860, 1595, 1490, 1335, 1310, 1245, 1115, 1045, 685. – ^{13}C-NMR. ($CDCl_3$): 139.8, 129.2, 122.8, 116.3, 91.5 (*d*, C(1)), 67.7 (*s*, C(5)), 39.0 (*t*, C(6)), 33.1 (*t*, C(8)), 24.8 (*qa*, CH_3), 24.4 (*t*, C(7)).

5-Phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (**17c**, **d**). From norbornene (**9**), 80% of **17c**, **d**, m.p. 99–100° ([16a] m.p. 100–101°). – IR. (CCl_4): 2980, 2885, 1600, 1500, 1490, 1335, 1130, 1105, 1095, 1030, 980, 910, 685. – ^{13}C-NMR. ($CDCl_3$): 140.4 (*s*, C(1')), 129.2 (*d*, C(2')), 121.7 (*d*, C(4')), 113.9 (*d*, C(3')), 86.1 (*d*, C(2)), 60.1 (*d*, C(6)), 41.1 and 39.9 (each *d*, C(1) and C(7)), 32.0 (*t*, C(10)), 25.4 and 24.7 (each *t*, C(8) and C(9)).

$C_{13}H_{15}N_3$ (213.29) Calc. C 73.21 H 7.09 N 19.70% Found C 73.33 H 7.32 N 19.82%

Mesitylisoxazolines from strained olefins and mesitonitrile oxide. – The olefins were dissolved in a solution of 1.05 mol-equiv. of mesitonitrile oxide[2] [27] in pentane and held at RT. for 2 h. The crude product obtained on evaporation i.V. was analyzed by NMR. Where possible, pure isomers were obtained on crystallization from pentane or petroleum ether. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.2–2.3 (*s*, 3 H and *s*, 6 H, not always separated, $ArCH_3$); 6.7–6.9 (broad *s*, 2 H, ArH). Other signals see *Table 2*.

4-Mesityl-2-oxa-3-azatricyclo[6.3.1.0^{1,5}]dodec-3-ene (**10e**) *and 2-mesityl-4-oxa-3-azatricyclo-[6.3.1.0^{1,5}]dodec-2-ene* (**10f**). From bicyclo[3.3.1]non-1-ene (**2**) as a mixture of **10e** and **10f** (90:10), m.p. 85–88°. – IR. (CCl_4): 2930, 2860, 1610, 1460, 1450, 1440, 1375, 1335, 1315, 1065, 955, 910, 885, 865, 845. – MS.: 283 (M^+, 62%), 240 (100%). Decomposition was noted on attempted recrystallization.

4-Mesityl-2-oxa-3-azatricyclo[5.4.1.0^{1,5}]dodec-3-ene (**11e**) *and 2-mesityl-4-oxa-3-azatricyclo[5.4.1.0^{1,5}]-dodec-3-ene* (**11f**). From bicyclo[4.2.1]non-1(8)-ene (**3**) as a mixture of **11e** and **11f** (77:23) (**11e**: m.p. 93–95°). – UV. (EtOH): 233 (3.85). – IR. (CCl_4): 2920, 2860, 1705, 1615, 1450, 1375, 1320, 910, 885, 875, 850. – ^{13}C-NMR. ($CDCl_3$) **11e**: 160.4 (*s*, C(4)), 138.2, 136.7, 128.7, 126.5, 96.9 (*s*, C(1)), 61.8

(*d*, C(5)), 41.7, 36.8, 35.9, 35.7 (*d*, C(7)), 33.2, 24.4, 23.6, 21.0 (*qa*, CH_3), 20.2 (*qa*, 2 C, CH_3). **11f**: 165.0 (*s*, C(2)), 97.6 (*d*, C(5)), 68.1 (*s*, C(1)), other signals only partially resolved. – MS.: 283 (M^+, 90%), 172 (100%).

$C_{19}H_{25}NO$ (283.42) Calc. C 80.52 H 8.89 N 4.94% Found C 79.81 H 9.06 N 4.96%

4-Mesityl-2-oxa-3-azatricyclo[7.2.1.0^{1,5}]dodec-3-ene (**12e**) *and 2-mesityl-2-oxa-3-azatricyclo[7.2.1.0^{1,5}]-dodec-2-ene* (**12f**). From bicyclo[4.2.1]non-1-ene (**4**) as a mixture of **12e** and **12f** (64:36). – IR. (CCl_4): 2975, 2920, 2860, 1610, 1450, 1375, 1310, 1150, 1130, 905, 850. – MS.: 283 (M^+, 41%), 254 (100%).

11-Mesityl-8-methyl-9-oxa-10-aza-trans-*bicyclo[6.3.0]undec-10-ene* (**13a**). From 1-methyl-(*E*)-cyclooctene (**5**), m.p. 81–82°. – IR. (KBr): 2925, 2860, 1615, 1600, 1570, 1450, 1370, 1305, 1080, 905, 890, 850, 815, 795, 735. – ^{1}H-NMR. ($CDCl_3$): 1.37 (*s*, CH_3), other signals *vide supra*. – ^{13}C-NMR. ($CDCl_3$): 162.9 (*s*, C(11)), 138.4, 137.4, 136.3, 128.6, 128.5, 126.8, 88.9 (*s*, C(8)), 56.6 (*d*, C(1)), 41.6, 29.6, 29.3, 27.8, 25.6, 24.7, 21.0 (*qa*, 2 C), 20.5 (*qa*), 19.8 (*qa*, CH_3–C(8)).

$C_{19}H_{27}NO$ (285.43) Calc. C 79.95 H 9.54 N 4.90% Found C 79.68 H 9.63 N 5.13%

5-Mesityl-2-methyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-4-ene (**14e**). From 2-methylnorborn-2-ene (**6**), decomposes at *ca.* 140°. – IR. (film): 2970, 2930, 2880, 1640, 1610, 1440, 1375, 1320, 1130, 1100, 895, 845, 830. – ^{13}C-NMR. ($CDCl_3$): 157.6 (*s*, C(5)), 138.3, 136.6, 128.7, 127.0, 93.0 (*s*, C(2)), 66.6 (*d*, C(6)), 47.5, 40.9 (each *d*, C(1) and C(7)), 35.4 (*t*, C(10)), 27.7, 23.5 (each *t*, C(8) and C(9)), 21.0 (*qa*, CH_3–C(2)), 20.8 (*qa*), 20.1 (*qa*, 2 C).

4-Mesityl-1-methyl-2-oxa-3-azabicyclo[3.3.0]oct-3-ene (**15e**). From 1-methylcyclopentene (**7**), decomposes on attempted recrystallization. – IR. (film): 2980, 2930, 2870, 1635, 1610, 1448, 1375, 890, 850, 815. – ^{1}H-NMR. ($CDCl_3$): 1.57 (*s*, CH_3), other signals *vide supra*. – ^{13}C-NMR. ($CDCl_3$): 158.4 (*s*, C(4)), 138.3 (*s*, C(1')), 136.9 (*s*, 2 C, C(2')), 128.7 (*d*, 2 C, C(3')), 126.8 (*s*, C(4')), 94.9 (*s*, C(1)), 61.4 (*d*, C(5)), 41.3 (*t*, C(8)), 30.9 (*t*, C(6)), 25.1 (*t*, C(7)), 24.8 (*qa*, CH_3–C(1)), 21.0 (*qa*, CH_3–C(4')), 19.9 (*qa*, 2 C, CH_3–C(2')).

3-Mesityl-4,5,5-trimethyl-1-oxa-2-azacyclopent-2-ene (**16e**). From 2-methylbut-2-ene (**8**), decomposes on attempted recrystallization. – IR. (film): 2970, 2930, 2870, 1640, 1610, 1450, 1375, 1325, 870, 850. – ^{1}H-NMR. ($CDCl_3$): 0.95 (*d*, CH_3–C(4)), 1.34 and 1.51 (each *s*, CH_3–C(5)), other signals *vide supra*. – ^{13}C-NMR. ($CDCl_3$): 161.7 (*s*, C(3)), 138.4, 137.0, 128.7, 126.5, 88.7 (*s*, C(5)), 53.7 (*d*, C(4)), 27.7 (*qa*, *trans*-CH_3–C(5)), 21.5 (*qa*, *cis*-CH_3–C(5)), 21.0 (*qa*, CH_3–Ar), 20.1 (*qa*, 2 C, CH_3–Ar), 11.0 (*qa*, CH_3–C(4)).

5-Mesityl-3-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-4-ene (**17e**, **f**). From norbornene (**9**), 92% of **17e**, **f**, m.p. 97.5–98.5°. – UV. (EtOH): 230 (3.8). – IR. (CCl_4): 2955, 2920, 2870, 1610, 1570, 1447, 1372, 1321, 1310, 915, 895, 880, 845. – ^{13}C-NMR. ($CDCl_3$): 157.5 (*s*, C(5)), 138.2, 136.6, 128.7, 126.6, 86.7 (*d*, C(2)), 61.3 (*d*, C(6)), 42.8 and 38.9 (each *d*, C(1) and C(7)), 32.8 (*t*, C(10)), 27.6 and 22.8 (each *t*, C(8) and C(9)), 20.9 (*qa*), 20.1 (*qa*, 2 C).

$C_{17}H_{21}NO$ (255.36) Calc. C 79.96 H 8.29 N 5.44% Found C 80.11 H 8.38 N 5.49%

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