Stereoselectivity of the Thermally Initiated Free-Radical Chain Addition of Cyclohexane to 1-Alkynes

Jürgen O. Metzger* and Michael Blumenstein

Fachbereich Chemie der Universität Oldenburg,
Carl-von-Ossietzky-Straße 9–11, D-26111 Oldenburg, F.R.G.

Received June 11, 1993

Key Words: Radicals / Addition / Stereoselectivity / Alkynes

Alkanes can be added to alkynes in a thermally initiated free-radical chain reaction ("ane reaction"). The addition of cyclohexane to 1-alkynes **1a–l** yields a mixture of (*Z*)- and (*E*)-2-cyclohexyl-1-alkenes **3a–l**. An essential step in this reaction is the addition of cyclohexyl radicals to the alkynes to give 2-cyclohexyl-1-alkenyl radicals **2a–l** which abstract hydrogen from cyclohexane to yield the products **3a–l**. The stereoselectivity of the addition has been measured in the temperature range of 160–260°C. It strongly depends on the substituent X of the radical center and varies over a range of almost four orders of magnitude from [(*Z*)-**3a**]:[(*E*)-**3a**] = 33 (X = OMe) at 160°C to [(*Z*)-**3l**]:[(*E*)-**3l**] = 0.012 (X = *t*Bu) at 260°C. The stereoselectivity is further influenced by the temperature and in most cases by the concentration of the hydrogen donor cyclohexane. The reaction is discussed in terms of the stereoselectivity of the addition of cyclohexyl radicals to the alkyne, of the structure of the 1-alkenyl radical (σ and π radical, respectively), the rate of inversion in the case of σ alkenyl radicals, and the relative rates of *syn* and *anti* hydrogen transfer.

Alkanes can be added to alkenes in a thermally initiated free-radical chain reaction (ane reaction)[1,2]. The radical chain is initiated by a molecule-induced homolysis[3] of alkane and alkene to give two alkyl radicals[4]. The ane reaction can also be applied to alkynes. Thus, cyclohexane has been added to acetylene at 400°C and a pressure of 400 bar to give vinylcyclohexane[5].

Free-radical additions to alkynes have been reviewed[6]. There are only relatively few examples of the intermolecular addition of carbon-centered radicals to alkynes[6a,7]. The stereochemistry of free-radical additions to alkynes has been discussed and reviewed[8–10]. In the first step, free radicals attack the triply bonded carbon perpendicularly to the acetylenic bond to form an electron-paired σ linkage and an alkenyl radical at the adjacent carbon. It has been shown by ESR spectroscopy that 1-alkenyl radicals can be characterized as either "bent" σ radicals (X = H, alkyl, Hal, OMe) or as "linear" π radicals (X = Ph, CO_2R, CN)[11]. However, the conclusion that the latter 1-alkenyl radicals are π radicals has been questioned[12,13]. Muon spin rotation spectroscopy confirmed the conclusion that 1-alkenyl radicals with X = Ph, $SiMe_3$ are linear π radicals[14].

In the case of linear π radicals, for example **2**, the ratio of the stereoisomeric product is determined exclusively by the stereochemistry of the hydrogen transfer to the 1-alkenyl radicals. Because the approach of the hydrogen donor from the *anti* side of the 1-alkenyl radicals (away from the β substituent) requires less activation enthalpy than the attack from the *syn* side, a hydrogen atom is transferred normally preferentially *anti* with respect to the β substituent to give the thermodynamically more instable *cis*-alkene[8,15].

In the case of σ alkenyl radicals the stereoselectivity is more complicated. It has been shown experimentally[16,17] and by ab initio calculations[18] that the free-radical addition to an alkyne **1** affords a (*Z*)-alkenyl radical, for example (*Z*)-**2**. Synchronously to the formation of the new bond, the remaining odd-electron orbital, which is situated at the adjacent carbon, is forced to occupy a position opposite to the direction of the attacking free radical due to stereoelectronic requirements[6b]. If the hydrogen transfer step is much faster than inversion to the (*E*)-alkenyl radical (*E*)-**2**, then kinetically controlled *anti* addition products (*Z*)-**3** are formed[16]. But if the rate of the hydrogen transfer step is comparable to the rate of inversion, the *syn* and *anti* addition products **3** are formed, depending on the relative rates of inversion and *syn* and *anti* hydrogen transfer. Finally, if the hydrogen transfer is much slower than inversion, equilibrations of (*Z*)- and (*E*)-alkenyl radicals can be reached, and the difference of stability of the two stereoisomeric radicals and the relative rates of *syn* and *anti* hydrogen transfer are now important for the stereochemical outcome of the addition reaction. Steric effects play a dominant role making the radical (*E*)-**2** more stable than the corresponding radical (*Z*)-**2**. The relative rates of *syn* and *anti* hydrogen transfer are also influenced by steric effects[8,10].

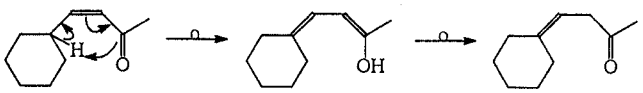
We have shown that the ane reaction is suitable to study the stereoselectivity of free-radical additions of cyclohexane to phenylacetylene[15]. We have now investigated the stereoselectivity of the thermally initiated free-radical addition of cyclohexane to 1-alkynes **1** via alkenyl radicals **2** to give 1,2-disubstituted alkenes **3**. Some preliminary results have been reported[19].

Results

Cyclohexane was allowed to react in the absence of air with the alkynes **1** (ratio 500–1000:1) in the temperature range from 160 to 260°C. The addition products **3** were

  0009–2940/93/1111–2493 $ 10.00+.25/0

formed with high regioselectivity. The cyclohexyl group is added preferentially to the unsubstituted terminus of the C,C triple bond[20]. For example, in the case of methyl propiolate (**1d**) the ratio of the regioisomeric addition products **3d** to methyl 2-cyclohexylacrylate was 21:1[21]. The reaction time was chosen such that the conversion (<10%) sufficed for the determination of the stereoisomeric ratio of the products by capillary gas chromatography. No (*Z*) to (*E*) isomerization of the products could be detected by variation of the reaction time and conversions of up to 50%. However, a [1,5]-sigmatropic rearrangement of product (*Z*)-**3c** was observed[22].



(*Z*)-**3c**

All the products **3** were unambiguously identified by a comparison with authentic compounds or isolation of the products and characterization by ^{1}H-NMR spectroscopy. The reaction could also be performed on a preparative scale.

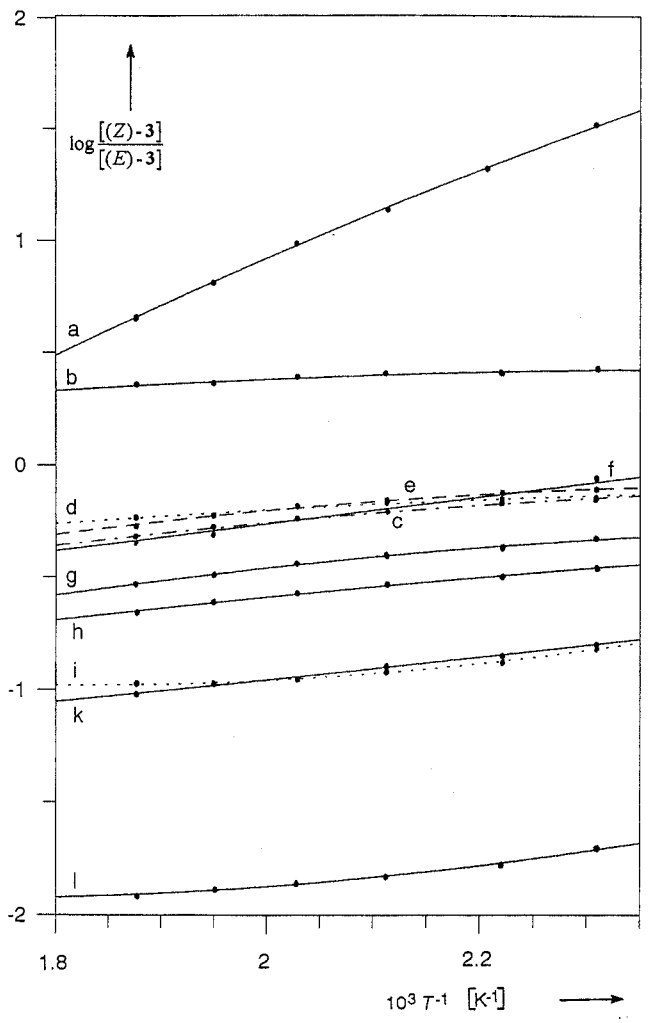


Figure 1. Temperature dependence of the addition of cyclohexane to 1-alkynes **1**

In that case the alkynes and cyclohexane were allowed to react in an autoclave for several hours. In most cases, only some minor products had to be removed by chromatography or distillation, and the stereoisomeric product mixture **3** could easily be obtained.

To prove the dependence of the stereoselectivity on the concentration of cyclohexane, the alkynes were allowed to react with mixtures of cyclohexane and benzene, the latter solvent being inert in the ane reaction[1]. The concentration of cyclohexane varied from 2 to 6 M. The results are compiled in Figures 1 and 2. It is remarkable that the stereoselectivity varies over a range of almost four orders of magnitude. There are cases with almost exclusive formation of (*Z*)-**3a** (X = OMe) and others with almost exclusive formation of (*E*)-**3l** (X = *t*Bu).

In most cases, the ratio of the stereoisomeric products [(*Z*)-**3**]:[(*E*)-**3**] decreases linearly with decreasing concentra-

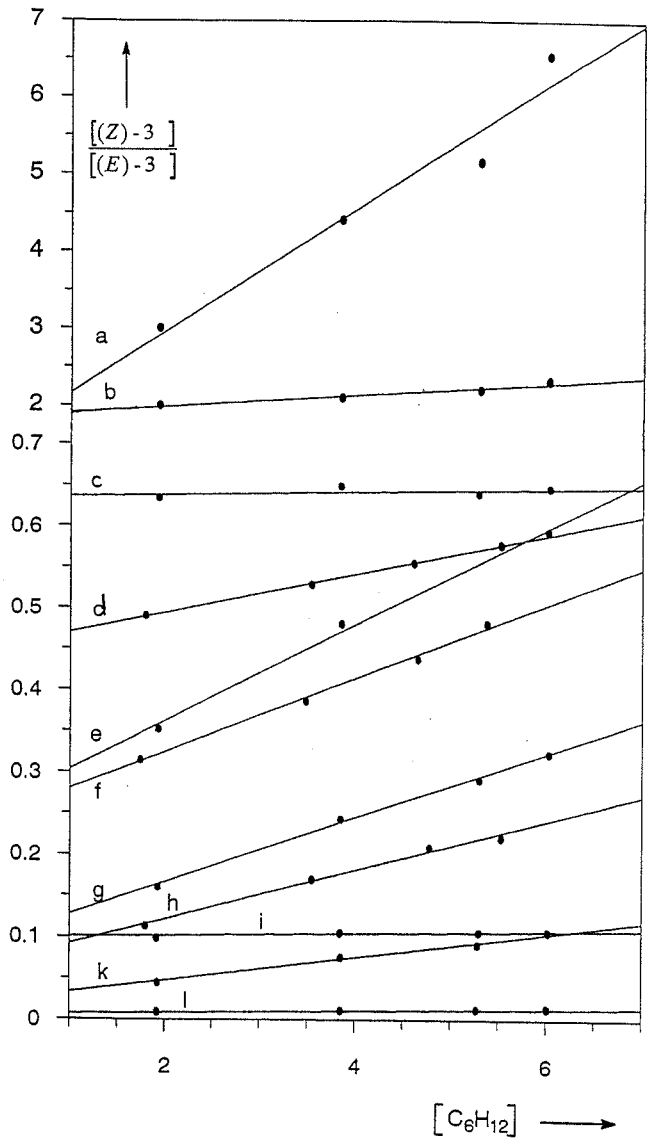


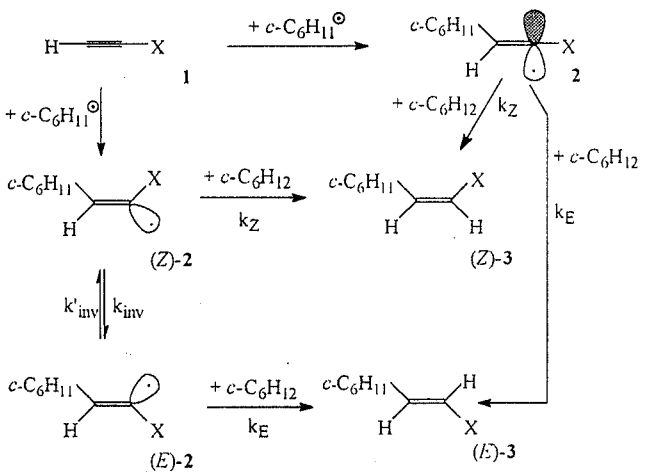
Figure 2. Dependence of the ratio of the addition products [(*Z*)-**3**]:[(*E*)-**3**] on the concentration of the hydrogen donor cyclohexane at 240°C (The ratio of the addition products to the alkynes **1d**, **1f**, and **1h** was measured at 260°C.)

tion of the hydrogen donor cyclohexane with the exception of X = COMe, $SiMe_3$, *t*Bu (Figure 2). The ratio of [(*Z*)-**3**] to [(*E*)-**3**] decreases with increasing temperature in all cases (Figure 1). (*E*)-**3** is formed preferentially in most cases, and the stereoselectivity increases with rising temperature. However, (*Z*)-**3** is formed preferentially if X = CN, OMe, and the stereoselectivity decreases with increasing temperature.

Discussion

The kinetics expected to be involved in the reaction sequence is illustrated by Scheme 1. The addition products (*Z*)-**3** and (*E*)-**3** are formed in a competition reaction by hydrogen transfer from cyclohexane to the alkenyl radicals **2**. Radicals **2** are formed by the addition of cyclohexyl radicals to alkynes **1**. The free-radical chain reaction is initiated by molecule-induced homolysis of cyclohexane and alkyne **1**[4]. Depending on the structure of the formed alkenyl radical **2** – either a bent σ or a linear π radical – different competition kinetic schemes are to be expected[8].

Scheme 1



1 - 3	a	b	c	d	e
X	OMe	CN	COMe	COOMe	Me

1 - 3	f	g	h	i	k	l
X	Ph	Et	*n*-Bu	$SiMe_3$	*c*-C_6H_{11}	*t*-Bu

Bent σ Alkenyl Radicals 2

In the addition step (*Z*)-**2** is formed[16,17] due to stereoelectronic requirements[6b]. Competition between hydrogen transfer and inversion gives product (*Z*)-**3** and radical (*E*)-**2**, respectively. Radical (*E*)-**2** can be trapped by hydrogen transfer to give (*E*)-**3** in competition with inversion back to radical (*Z*)-**2**. The ratio of the addition products is given by the competitive kinetic equation (1) and is expected to depend on the concentration of the hydrogen donor. The ratio of [(*Z*)-**3**]:[(*E*)-**3**] should decrease linearly with decreasing concentration of the hydrogen donor. A nonlinear relative Arrhenius relationship of the ratio [(*Z*)-**3**]:[(*E*)-**3**] should be observed[8].

$$\frac{[(Z)\text{-}3]}{[(E)\text{-}3]} = \frac{k_Z \cdot k'_{inv}}{k_E \cdot k_{inv}} + \frac{k_Z[c\text{-}C_6H_{12}]}{k_{inv}} \quad (1)$$

Two borderline cases should be discussed: If inversion is fast relative to radical scavenging, the second term of equation (1) approaches zero, and the product ratio is determined by equation (2) and the Curtin-Hammett principle has to be applied. A linear Arrhenius relationship with a positive or negative slope is expected because $\Delta H^{\neq}_{(Z)} - \Delta H^{\neq}_{(E)} < 0$, whereas $\Delta H^{0}_{(Z)} - \Delta H^{0}_{(E)} > 0$[8].

$$\frac{[(Z)\text{-}3]}{[(E)\text{-}3]} = \frac{k_Z \cdot k'_{inv}}{k_E \cdot k_{inv}} \quad (2)$$

However, if the inversion is slow relative to radical scavenging, the product ratio is determined by the second term of equation (1) and equation (3) should apply. In this case, a linear relative Arrhenius relationship is to be expected, and the ratio of [(*Z*)-**3**]:[(*E*)-**3**] greatly depends on the concentration of cyclohexane.

$$\frac{[(Z)\text{-}3]}{[(E)\text{-}3] \cdot [c\text{-}C_6H_{12}]} = \frac{k_Z}{k_{inv}} \quad (3)$$

Linear π Alkenyl Radicals 2

In the case of linear π radicals the ratio of the stereoisomeric products should be determined exclusively by the ratio of the hydrogen transfer rate constants given in equation (4).

$$\frac{[(Z)\text{-}3]}{[(E)\text{-}3]} = \frac{k_Z}{k_E} \quad (4)$$

A linear relative Arrhenius relationship with a positive slope is assumed. The slope should be more positive than in the case of equation (2). The ratio of the products should be independent of the concentration of the hydrogen donor.

Applying equations (1)–(4) to the experimental results given in Figures 1 and 2, we can observe and differentiate in most cases all the possibilities discussed above.

Addition of Cyclohexane to Methoxyacetylene (1a)

A configurationally very stable 1-methoxyalkenyl radical (*Z*)-**2a** is formed by the addition of cyclohexyl radical to alkyne **1a**[16]. Equation (3) can be applied (Figure 3), and the relative Arrhenius parameters of hydrogen transfer and inversion of radical (*Z*)-**2a** are obtained. The differences of the activation enthalpies and activation entropies are $\Delta H^{\neq}_{inv} - \Delta H^{\neq}_{(Z)} = 32$ kJ mol^{-1} and $\Delta S^{\neq}_{inv} - \Delta S^{\neq}_{(Z)} = 61$ J mol^{-1} K^{-1}, respectively.

Unfortunately, there are no reliable values of rate constants and activation parameters for hydrogen transfer reactions to alkenyl radicals available. However, it can be assumed that alkenyl radicals are more reactive than the

respective alkyl radicals. Assuming an activation enthalpy $\Delta H^{\neq}_{(Z)} \approx 40$ kJ mol^{-1}, we can estimate an inversion barrier of radical (*Z*)-**2a** of approximately 70 kJ mol^{-1}. The difference of the activation entropies of inversion and hydrogen transfer leads to a reasonable ratio of the *A* factors of $\log(A_{inv}:A_Z) = 3.2$[24].

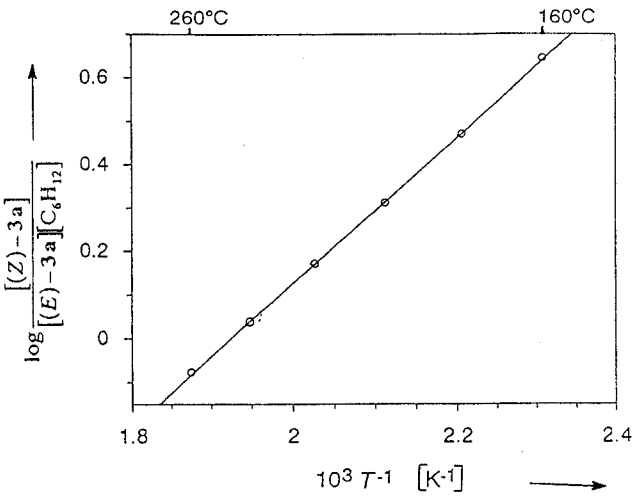


Figure 3. Temperature dependence of the stereoselectivity of the addition of cyclohexane to methoxyacetylene (**1a**) applying equation (3)

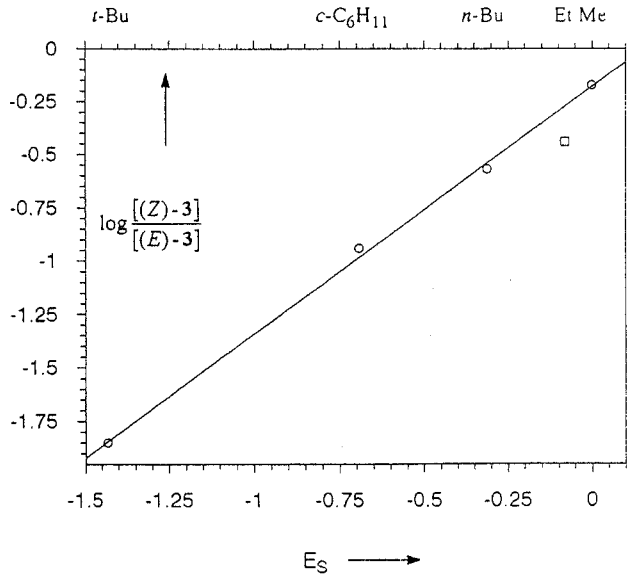


Figure 4. Correlation of the stereoselectivitiy of the addition of cyclohexane to 1-alkynes **1e**, **1g**, **1k**, **1l** (240°C), and **1h** (260°C) with steric substituent constants E_S of the alkyl substituents

Addition of Cyclohexane to Propyne (1e), 1-Butyne (1g), 1-Hexyne (1h), Cyclohexylethyne (1k), and 3,3-Dimethyl-1-butyne (1l)

The addition of cyclohexyl radical to these alkynes gives the σ alkenyl radicals (*Z*)-**2**. It can clearly be seen from Figure 2 and Table 1 that the ratio of $k_Z:k_{inv}$ given by the slope of the respective straight lines decreases with increasing steric effect of the alkyl substituent X (Me < Et < Bu < *c*-C_6H_{11} < *t*Bu) (Table 1). We assume that this effect is essentially due to the increasing rate of inversion of alkenyl radical (*Z*)-**2**. In the case of radical **2l** (X = *t*Bu) the ratio of the products [(*Z*)-**3**]:[(*E*)-**3**] seems to be independent of the concentration of cyclohexane, and equation (2) holds. With increasing steric demand of substituent X the rate constant of reverse inversion k'_{inv} decreases. Thus, the first term of equation (1) decreases, and more (*E*)-**3** is formed, and the stereoselectivity is nicely correlated with the steric substituent constant E_S[23] of substituent X (Figure 4). The ratio of the rate constants of hydrogen transfer $k_Z:k_E$ may also be influenced by the steric effect of substituent X. This effect, however, seems to be relatively small compared to the effect on the inversion rates as can be deduced from the ratio $k_E:k'_{inv}$ which increases with increasing steric effect of substituent X (Table 1).

Table 1. Ratio of the stereoisomers and relative kinetic data of the addition of cyclohexane (6.02 M) to alkyl-substituted acetylenes at 240°C

3	$\frac{[Z]\text{-}3}{[E]\text{-}3}$	$\frac{k_Z \cdot k'_{inv}}{k_E \cdot k_{inv}}$	$\frac{k_Z}{k_{inv}}$	$\frac{k_E}{k'_{inv}}$
e	0.596	0.247	0.057	0.23
g	0.324	0.088	0.039	0.44
h[a]	0.223	0.062	0.030	0.48
k	0.106	0.019	0.014	0.73
l	0.013	0.013	–	–

[a] 260°C; [*c*-C_6H_{12}] = 5.53 M.

Additions of Cyclohexane to Alkynes Cyanoethyne (1b), 3-Butyn-2-one (1c), Methyl Propiolate (1d), Phenylethyne (1f), and (Trimethylsilyl)ethyne (1i)

The alkenyl radicals **2** formed by the addition of cyclohexyl radicals to these alkynes may be π radicals, because the odd electron can be delocalized[11]. As already discussed, ESR[11] and Muon spin rotation[14] gave clear evidence that 1-phenylalkenyl radicals such as **2f** and 1-(trimethylsilyl)alkenyl radicals such as **2i** are π radicals. Kinetic measurements revealed that radical **1d** is a σ radical[13]. The ESR results seem to be ambiguous, and the problem is open to discussion[12]. ESR spectroscopy gave evidence that 1-cyanoalkenyl radicals such as **2b** are linear at 77 K. However, a bent 1-cyanoalkenyl radical could be trapped and measured by ESR at 4 K[8]. Radicals **2c** have obviously not been investigated previously by spectroscopic methods.

In the case of π radicals equation (4) should be fulfilled, and the product ratio should be independent of the concentration of the hydrogen donor. However, only in the case of the addition of cyclohexane to alkynes **1c** and **1i** was the stereoselectivity independent of the hydrogen donor concentration indicating that the respective radicals could be linear π radicals, whereas in the case of alkynes **1b**, **1d**, and **1f** a dependence of stereoselectivity on the hydrogen donor concentration was observed. This is a surprising and remarkable result. To explain these effects we assume that the enthalpy differences between the respective σ and π radicals are rather low in the cases of the 1-alkenyl radicals **2b**, **2d**, and **2f** as indicated by AM1 calculations, which show a very

broad range of approximately equal energy of linear and bent radicals. The enthalpy difference should be the resonance energy of the respective π radical. Resonance energies of alkenyl radicals are not known but they should not exceed the respective values of alkyl radicals. However, the entropy of a π radical such as **2d** and **2f** is expected to be approximately 22 J mol^{-1} K^{-1} lower than that of the respective σ radical because of restricted rotation of substituent X and the higher symmetry of the π radical[24b]. At elevated reaction temperatures of 240 and 260°C (Figure 2), the free energy ΔG^0 of the σ radical could easily be lower than that of the respective π radical because of entropy effects, also if the ground state at room temperature may be a stabilized π radical. Thus, with decreasing temperature and decreasing entropy effects a change from σ to π alkenyl radical may occur. Experimental evidence has been obtained in the case of alkyne **1d**. The dependence of the ratio of [(*Z*)-**3d**]:[(*E*)-**3d**] on the concentration of the hydrogen donor cyclohexane decreases with decreasing temperature (Figure 5). An explanation of this surprising result could be the entropy effect discussed above.

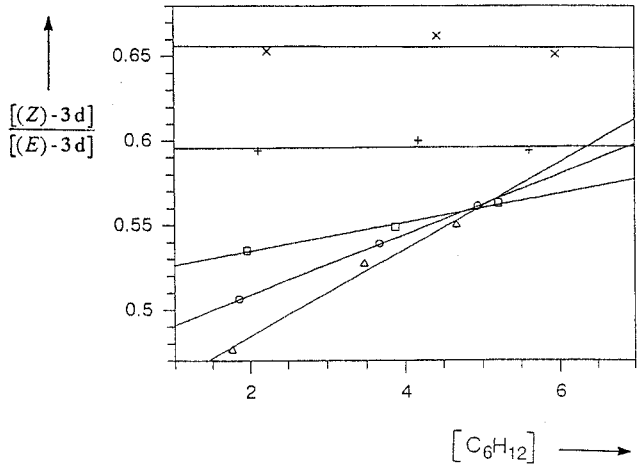


Figure 5. Dependence of the ratio of the addition products [(*Z*)-**3d**]:[(*E*)-**3d**] on the concentration of the hydrogen donor cyclohexane from 200 to 260°C. ×: 200°C, +: 220°C, □: 240°C, ○: 250°C, △: 260°C

Thus, our results give additional evidence[12,13] that 1-alkenyl radicals **2b**, **2d**, and **2f** could be bent at least at elevated temperatures up to 260°C, whereas 1-alkenyl radicals **2c** and **2i** are linear.

This work was supported by the *Deutsche Forschungsgemeinschaft*. We are greatly indebted to Prof. *H. Hopf* and Dipl.-Chem. *B. Witulski*, TU Braunschweig, Germany, for kindly providing a sample of cyanoethyne and Prof. *B. Giese* and Dipl.-Chem. *W. Damm*, Basel, Switzerland, for introducing us in the handling of AM1. Technical assistance by Mr. *F. Bangert* is gratefully acknowledged.

Experimental

^1H and ^{13}C NMR: Bruker AM 300; solvents $CDCl_3$ and C_6D_6; internal standard tetramethylsilane (TMS). – MS: Finnigan MAT 212 (for GC/MS coupled with a Varian 3700). – Analytical GC: Carlo Erba GC 6000 Vega Series 2 with FID detector, fused silica capillary column DB1 30 m. – Liquid chromatography: Merck silica gel 60, 0.04–0.063 mm. – Autoclave: High-grade steel tube with a volume of 140 ml. – Solvents were purified and dried in the usual way.

Starting Materials **1**: Alkynes **1c–l** were commercially available and were purified by distillation. Cyanoethyne (**1b**) was obtained from B. Witulski and H. Hopf, Institut für Organische Chemie, TU Braunschweig, Germany. Methoxyacetylene (**1a**) was best prepared from 2-chloroacetaldehyde dimethyl acetal by a method described by Brandsma[25].

Competitive Kinetic Measurements: The reactions of the alkynes **1a–l** with cyclohexane were carried out in vacuum-sealed Duran glass ampoules (outer diameter 7 mm, inner diameter 4 mm, length 170 mm, volume 2.1 ml). The solutions (0.01 M **1**) were deoxygenated by 3–4 freeze-thaw cycles. For each measurement three ampoules were used to carry out the reaction at constant temperature in an oil bath (Haake N4-B; ±0.01°C). The solutions were analyzed directly by GC. The products were identified by a comparison of the retention times of independently synthesized reference compounds. *n*-Dodecane was used as internal standard.

Addition Products **3** are described in the literature with the exception of **3l**. They were indepenently synthesized by thermal addition of cyclohexane to the respective alkyne on a preparative scale or by adapted literature procedures.

1-Cyclohexyl-2-methoxyethene (**3a**): 5.0 g (11.5 mmol) of (methoxymethyl)triphenylphosphonium bromide/sodium amide in 30 ml of THF was stirred under N_2 for 15 min. To this suspension 2 ml (15 mmol) of cyclohexanecarbaldehyde was added. After stirring for 60 min at room temp., 60 ml of water was added, and the solution was extracted with diethyl ether. The organic layer was separated, dried with $MgSO_4$, and concentrated. Bulb-to-bulb distillation of the residue gave 1.5 g of a product (yield 93% based on the ylide) containing 70% of (*E*)-**3a** and about 30% of (*Z*)-**3a**. The ^1H-NMR data corresponded in all respects with the compound described in ref.[26]

1-Cyano-2-cyclohexylethene (**3b**): A solution of 11.69 g (66 mmol) of diethyl cyanomethylphosphonate in 50 ml of THF was added under N_2 to a solution of 2.73 g (70 mmol) of sodium amide in 75 ml of THF. After stirring for 8 h at room temp., 4.0 g (36 mmol) of cyclohexanecarbaldehyde dissolved in 150 ml of THF was added. After 18 h the solution was hydrolyzed with 120 ml of water, concentrated, and the separated aqueous layer was extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated. The resulting crude product was purified by bulb-to-bulb distillation. Yield: 4.76 g (98%) containing 60% of (*E*)-**3b** and 40% of (*Z*)-**3b**; b.p. 191–193°C. The ^1H-NMR data corresponded in all respects with the compound described in ref.[27]

4-Cyclohexyl-3-buten-2-one (**3c**): 0.68 g (10 mmol) of 3-butyn-2-one and 2.8 g (10 mmol) of cyclohexylmercury chloride were dissolved in 200 ml of dichloromethane. Then a solution of 3.0 g (80 mmol) of $NaBH_4$ in 4 ml of water was added. After 15 min, the solution was dried with $MgSO_4$, and the filtrate was subjected to bulb-to-bulb distillation to give 180 mg (12%) of **3c** ([*E*)-**3c**]:[(*Z*)-**3c**] = 2.5:1). – ^1H NMR (C_6D_6): δ = 0.8–2.0 (m, 22H, *E,Z*-C_6H_{11}), 1.8 (s, 3H, *Z*-CH_3), 1.9 (s, 3H, *E*-CH_3), 5.51 (dd, 1H, *Z*- =CHC_6H_{11}), 5.65 (d, 1H, *Z*- =$CHCOCH_3$), 5.85 (dd, 1H, *E*- =$CHCOCH_3$), 6.46 (dd, 1H, *E*- =CHC_6H_{11}); $J(Z)_{1,2}$ = 11.5, $J(E)_{1,2}$ = 16.1, $J(Z)_{1,1'}$ = 9.6, $J(E)_{1,1'}$ = 6.8, $J(E)_{1',2}$ = 1.2 Hz. – MS (**3c**) (EI, 70 eV), *m/z* (%): 152 (22) [M^+]. – The compound is described in ref.[28]

Methyl 3-Cyclohexylacrylate (**3d**) was prepared as described in refs.[29,30]

1-Cyclohexyl-1-propene (**3e**): 80 ml of cyclohexane was saturated with propyne, and the mixture was heated under N_2 for 8 h in an autoclave at 250°C. Bulb-to-bulb distillation gave 70 mg of **3e** ([(*E*)-**3e**]:[(*Z*)-**3e**] = 1.6:1). The ^{1}H-NMR data correspond with the compound described in ref.[31]

1-Cyclohexyl-2-phenylethene (**3f**): A mixture of 80 ml of cyclohexane and 80 mg (0.78 mmol) of phenylethyne was heated for 8 h in an autoclave at 240°C under N_2. Cyclohexane was removed, and the residue was subjected to column chromatography yielding 88 mg (61%) of **3f** ([(*E*)-**3f**]:[(*Z*)-**3f**] = 1.6:1). The compound is described in refs.[29,32]

1-Cyclohexyl-1-butene (**3g**): 80 ml of cyclohexane was saturated with 1-butyne and the mixture heated unter N_2 in an autoclave for 8 h at 250°C. Cyclohexane was removed, and column chromatography of the residue yielded 80 mg of **3g** ([(*E*)-**3g**]:[(*Z*)-**3g**] = 3:1). The compound is described in ref.[33] – ^{1}H NMR ($CDCl_3$): δ = 1.0 (t, 3H, *E*-CH_3), 1.25 (t, 3H, *Z*-CH_3), 1.4–1.8 (m, 22H, *E,Z*-C_6H_{11}), 2.0 (m, 2H, *E*-CH_2CH_3), 2.28 (m, 2H, *Z*-CH_2CH_3), 5.35 (m, 4H, *E,Z*-CH=C*H*).

1-Cyclohexyl-1-hexene (**3h**): A mixture of 80 ml of cyclohexane and 82 mg (1 mmol) of 1-hexyne was heated for 8 h in an autoclave at 250°C under N_2. Cyclohexane was removed, and bulb-to-bulb distillation of the residue yielded 90 mg (54%) of **3h** ([(*E*)-**3h**]:[(*Z*)-**3h**] = 5:1]. The ^{1}H-NMR data corresponded with the compound described in ref.[34]

1-Cyclohexyl-2-(trimethylsilyl)ethene (**3i**): A mixture of 80 ml of cyclohexane and 250 mg (2.5 mmol) of (trimethylsilyl)ethene was heated for 8 h in an autoclave at 230°C under N_2. Cyclohexane was removed, and column chromatography of the residue yielded 80 mg (18%) of **3i** ([(*E*)-**3i**]:[(*Z*)-**3i**] = 16:1]. The ^{1}H-NMR data corresponded with the compound described in ref.[35]

1,2-Dicyclohexylethene (**3k**): A mixture of 80 ml of cyclohexane and 549 mg (5 mmol) of cyclohexylethyne was heated for 8 h in an autoclave at 250°C under N_2. Cyclohexane was removed, and column chromatography of the residue yielded 120 mg (18%) of **3k** ([(*E*)-**3k**]:[(*Z*)-**3k**] = 8:1]. **3k** is described in ref.[36] However, the ^{1}H-NMR data of (*E*)-**3k** given in ref.[36a] correspond with the compound (*Z*)-**3k**. – ^{1}H NMR ($CDCl_3$): δ = 0.8–2.8 (m, 44H, *E,Z* 2 C_6H_{11}), 5.09 (dd, 2H, *Z*-$C_6H_{11}CH$=), 5.30 (dd, 2H, *E*-$C_6H_{11}CH$=); $J(Z)_{1,1'}$ respect. $J(Z)_{2,1''}$ = 6.4, $J(E)_{1,1'}$ respect. $J(E)_{2,1''}$ = 3.5, $J(Z)_{1,1''}$ respect. $J(Z)_{1',2}$ = 1.9, $J(E)_{1,1''}$ respect. $J(E)_{1',2}$ = 1.7 Hz. – ^{13}C NMR ($CDCl_3$): δ = 26–44 (24 s, 24 C, *Z,E* 2 C_6H_{11}), 133.76 (s, *E*-CH=), 134.20 (s, *Z*-CH=).

(E)-1-Cyclohexyl-3,3-dimethyl-1-butene [(*E*)-**3l**]: A mixture of 70 ml of cyclohexane and 250 mg (3 mmol) of 3,3-dimethyl-1-butyne was heated for 9 h in an autoclave at 250°C under N_2. Cyclohexane was removed, and column chromatography of the residue furnished 50 mg (10%) of **3l**. – ^{1}H NMR ($CDCl_3$): δ_E = 0.9–2.0 [m, 20H, C_6H_{11}, $C(CH_3)_3$], 5.25 (dd, 1H, =C*H*C_6H_{11}), 5.41 [dd, 1H, =C*H*C$(CH_3)_3$]; $J_{1,2}$ = 15.8, $J_{1,1'}$ = 6.55, $J_{1',2}$ = 0.82 Hz. – ^{13}C NMR ($CDCl_3$): δ_E = 26.09, 26.18, 29.77, 32.43, 33.35, 40.68 [10 s, 10 C, C_6H_{11} und $C(CH_3)_3$], 130.75 (s, C-1), 138.87 (s, C-2). – GC-MS (*E*-**3l**) (EI, 70 eV), *m/z* (%): 166 (0.4) [M^+].

(Z)-1-Cyclohexyl-3,3-dimethyl-1-butene [(*Z*)-**3l**]: A mixture of 13.1 g (0.05 mol) of triphenylphosphane and 9.0 g (0.051 mol) of (bromomethyl)cyclohexane was heated for 2 h at 150°C under N_2. The product was washed with diethyl ether to afford 15.3 g (0.035 mol, 70%) of phosphonium salt with a melting point of 208°C. 14 g (0.032 mol) of the phosphonium salt was mixed with 1.25 g (0.032 mol) of sodium amide, and 80 ml of THF was added to the mixture. After stirring for 15 min, 2.76 g (0.032 mol) of pivaldehyde was added, and stirring was continued for 3 h. Filtration of the reaction mixture, concentration of the filtrate, and vacuum distillation of the residue afforded 180 mg (2%) of (*Z*)-**3l**. – ^{1}H NMR ($CDCl_3$): δ_Z = 0.8–1.7 [m, 20H, C_6H_{11}, $C(CH_3)_3$], 4.91 (dd, 1H, =C*H*C_6H_{11}), 5.15 [dd, 1H, =CHC(C*H*$_3)_3$]; $J_{1,2}$ = 11.9, $J_{1,1'}$ = 10.6, $J_{1',2}$ = 0.46 Hz. – ^{13}C NMR ($CDCl_3$): δ_Z = 25.99, 26.04, 31.51, 33.04, 33.59, 37.37 [10 s, 10 C, C_6H_{11} und $C(CH_3)_3$], 135.40 (s, C-1), 137.58 (s, C-2). – MS (*Z*-**3l**) (EI, 70 eV), *m/z* (%): 70 (100), 81 (42), 83 (90), 96 (8) [C_7H_{12}], 109 (31) [$M^+ - C(CH_3)_3$], 166 (6) [M^+]. – $C_{12}H_{22}$: calcd. 166.1722; found 166.1721 (MS-EI).

[1] J. Hartmanns, K. Klenke, J. O. Metzger, *Chem. Ber.* **1986**, *119*, 488–499.
[2] J. O. Metzger, *J. Prakt. Chem.* **1990**, *332*, 767–781.
[3] J. A. K. Harmony, *Methods Free Radical Chem.* **1974**, *5*, 101 to 176.
[4] J. O. Metzger, *Angew. Chem.* **1983**, *95*, 914; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 889.
[5] J. O. Metzger, P. Köll, *Angew. Chem.* **1979**, *91*, 75–76; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 71.
[6] Y. Amiel in S. Patai, Z. Rappoport, *The Chemistry of Functional Groups, Supplement C, The Chemistry of Triple Bonded Functional Groups*, Part 1, p. 341–382, Wiley, Chichester, **1983**. – [6a] *ibid.* p. 353–359. – [6b] *ibid.* p. 345–347.
[7] *Methoden Org. Chem. (Houben-Weyl), C-Radikale* (Eds.: M. Regitz, B. Giese), Bd. E 19a, **1989**; D. P. Curran, in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), vol. 4 (Ed.: M. F. Semmelhack), Oxford, **1991**, p. 715–778 and 779 to 831.
[8] L. A. Singer, *Sel. Org. Transform.* **1972**, *2*, 239–268.
[9] O. Simamura, *Top. Stereochem.* **1969**, *4*, 1–37.
[10] B. Giese, *Angew. Chem.* **1989**, 101, 993–1004; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 969–980.
[11] A. L. J. Beckwith, K. U. Ingold in *Rearrangement in Ground and Excited States* (Ed.: P. de Mayo), vol. 1, Academic Press, New York, **1980**, p. 280–310.
[12] H. G. Korth, J. Lusztyk, K. U. Ingold, *J. Chem. Soc., Perkin Trans 2*, **1990**, 1997–2007.
[13] O. Ito, R. Omori, M. Matsuda, *J. Am. Chem. Soc.* **1982**, *104*, 3934–3937.
[14] C. J. Rhodes, E. Roduner, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 1729–1733, and references cited.
[15] B. Giese, J. A. Gonzáles-Gómez, S. Lachhein, J. O. Metzger, *Angew. Chem.* **1987**, *99*, 475–476; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 479–480.
[16] D. K. Wedegaertner, R. M. Kopchik, J. A. Kampmeier, *J. Am. Chem. Soc.* **1971**, *93*, 6890–6895.
[17] T. Ohnuki, M. Yoshida, O. Simamura, *Chem. Lett.* **1972**, 797 to 801.
[18] C. Sosa, H. B. Schlegel, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1987**, *91*, 267–282.
[19] J. O. Metzger, M. Blumenstein, *Sixth International Symposium on Organic Free Radicals, Book of Abstracts*, Noordwijkerhout, The Netherlands, **1992**, p. 180–183.
[20] B. Giese, S. Lachhein, *Angew. Chem.* **1982**, *94*, 780–781; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 768–769.
[21] J. O. Metzger, K. Klenke, J. Hartmanns, D. Eisermann, *Chem. Ber.* **1986**, *119*, 508–513.
[22] T. L. Gilchrist, R. C. Storr, *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, **1979**, p. 249.
[23] J. A. MacPhee, A. Panaye, J.-E. Dubois, *Tetrahedron* **1978**, *34*, 3553–3562.
[24] S. W. Benson, *Thermochemical Kinetics*, Wiley, New York **1976**. – [24a] *ibid.* p. 104, 156. – [24b] *ibid.* p. 72.
[25] [25a] H. G. Viehe, *Chemistry of Acetylenes*, Marcel Dekker, New York, **1969**, p. 845. – [25b] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1988**, p. 174–175.
[26] [26a] G. Rousseau, P. Le Perchec, J. N. Conia, *Synthesis* **1978**, 67–70. – [26b] P. Magnus, G. Roy, *Organometallics* **1982**, *1*, 553–559.
[27] [27a] K. Furuta, M. Ishiguro, R. Haruta, N. Ikeda, H. Yamamoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768–2776. – [27b] G. Zweifel, J. T. Snow, C. C. Whitney, *J. Am. Chem. Soc.* **1968**, *90*, 7140.

[28] [28a] H. C. Brown, G. W. Kabalka, G. W. Holland, A. Suzuki, S. Nozawa, M. Itoh, *J. Am. Chem. Soc.* **1970**, *92*, 3503–3505. – [28b] T. Oritani, T. Matsunaga, K. Yamashita, *Agr. Biol. Chem.* **1973**, *37*, 261–268. – [28c] V. Theus, H. Schinz, *Helv. Chim. Acta*, **1956**, *155*, 1291–1298.
[29] S. Lachhein, Dissertation, Univ. Darmstadt, **1982**.
[30] R. C. Larock, *J. Org. Chem.* **1975**, *40*, 3237–3242.
[31] [31a] S. M. Neumann, J. K. Kochi, *J. Org. Chem.* **1975**, *40*, 599 to 606. – [31b] H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1975**, *97*, 5249–5255.
[32] G. M. Underwood, A. K. Chan, T. Green, C. T. Watts, C. A. Kingsbury, *J. Org. Chem.* **1973**, *38*, 2735–2746.
[33] H. Ishikawa, T. Mukaiyama, *Chem. Lett.* **1976**, 737–738.
[34] [34a] B. Singaram, T. E. Cole, H. C. Brown, *Organometallics* **1984**, *3*, 1523–1530. – [34b] J. B. Campbell, Jr., G. A. Molander, *J. Organomet. Chem.* **1978**, *156*, 71–79.
[35] R. B. Miller, G. McGarvey, *J. Org. Chem.* **1978**, *43*, 4424–4431.
[36] [36a] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fjioka, S. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969. – [36b] H. J. Bestmann, O. Kratzer, *Chem. Ber.* **1963**, *96*, 1899–1908.

[174/93]