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Photochemical Generation and Structure of Vinyl Radicals

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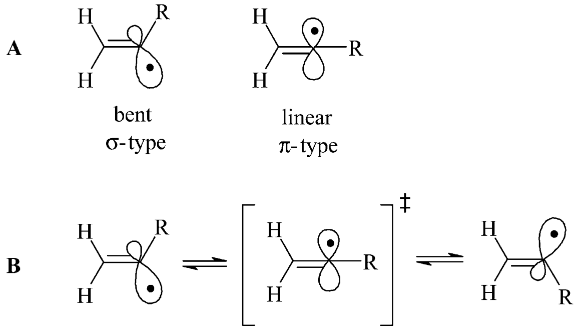
Photolysis of a series of *E* or *Z* stereoisomeric α-R-substituted bromostyrenes (R = CH_3, F or CN) in methanol yields *E* and/or *Z* stereoisomeric styrenes, which stem from the corresponding vinyl radicals. The results show that the α-Me vinyl radical is a rapidly equilibrating, bent structure, while the α-F vinyl radical is a stable bent species, in agreement with earlier thermal results. The α-CN vinyl radical is assigned as a rapidly inverting bent and not a linear species from the stereochemical results as a function of temperature. Stereochemical data for the α-C(H)=O system in diethyl ether indicate a stable bent vinyl radical as product forming species. The conclusions are supported by quantum chemical computations.

Introduction

Since the pioneering study of Stork and Baine[1] in 1982, vinyl radical reactions have developed into a versatile tool for synthetic organic chemists.[2] The structure of these radicals is a key factor in controlling the outcome of their reactions providing stereoisomeric products.[3] Vinyl radicals have either a bent or a linear structure, and are usually designated as σ- and π-type radicals, respectively (Scheme 1, A). These appellations refer to the presence or absence of any s-character in the singly occupied MO.



Scheme 1.

The configuration of vinyl radicals depends on the nature of the α-substituent R, and mainly two approaches have been used to deduce their structures.[4] The most straightforward method is evaluation of ESR hyperfine splitting constants. The other method is the generation of isomeric vinyl radicals from stereoisomeric *E* or *Z* α-substituted vinylic precursors or by addition of a radical to a carbon–carbon triple bond, and comparison of the product compositions after chemical trapping. Both approaches, however, suffer from drawbacks, which make it difficult to distinguish experimentally between a configurationally unstable,[5] rapidly inverting σ-type radical (Scheme 1, B), effectively linear, and a π-type, linear, vinyl radical.

Vinyl radicals with an α-hydrogen, -alkyl, -alkoxy, or -halogen substituent have since long been known to have a bent structure.[4] The α-silyl group induces a π-type, linear, vinyl radical structure.[6] The structures of vinyl radicals bearing unsaturated α-substituents that allow delocalization of the single electron are a topic of controversy. The cyano, carboxyl, phenyl and alkenyl group, for example, are all capable of π-delocalization and were thought to impose linearity on the radical center to effect maximum resonance stabilization. This assumption appeared to be corroborated by ESR data.[7] However, the linearity of α-carboxyl-,[8–10] α-phenyl-,[9,10] and α-cyano-substituted[10,11] vinyl radicals has been questioned.

Investigations of the structures of vinyl radicals by quantum chemical calculations also led to controversies and did not settle arguments. Guerra found that the α-ethynyl, α-cyano, and α-carboxyl substituent favor a bent vinyl radical structure, with a low inversion barrier, using the post-HF method UMP4/TZP.[12] The corresponding linear radicals were calculated to be transition states. In contrast, Galli, Mencarelli and co-workers calculated α-ethenyl, α-phenyl, α-cyano, and α-aldehyde-substituted vinyl radicals to have their minimum energy for a linear, π-type radical, with the single electron in conjugation with the α-π-electrons.[13] The latter authors used the DFT BLYP functional for their calculations, with a 6-31G(d,p) basis set. Similarly, the α-cyanovinyl radical is computed to have a bent structure using

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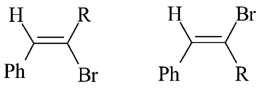
HF and post-HF methods, but a linear structure, using DFT methods.[14]

In this paper we report how, and to which extent, the photochemistry of vinyl halides can contribute to answering the question about the structure of α-substituted π- and σ-isomeric vinyl radicals. Upon irradiation, vinyl halides give two types of bond cleavage.[15] Heterolytic cleavage of the carbon–halogen bond yields vinyl cations, while homolytic cleavage leads to vinyl radicals. The cation to radical ratio depends on the nature of the α-substituent R as well as on the polarity of the solvent. The effects of a series of six α-substituents are considered: α-CH_3, α-F, α-CN, α-C(H)=O, α-C≡CH, and α-$CH=CH_2$. The compounds under experimental investigation are the *E* and *Z* isomeric bromostyrenes **1**–**6**. If these molecules undergo homolysis, they yield α-substituted β-phenyl vinyl radicals. When these radicals are bent, the stereoisomeric vinyl halides **a** and **b** initially generate two stereoisomeric, σ-type, radicals. If the resulting vinyl radical is linear, **a** and **b** produce the same π-type radical intermediate.



1a–**6a** **1b**–**6b**

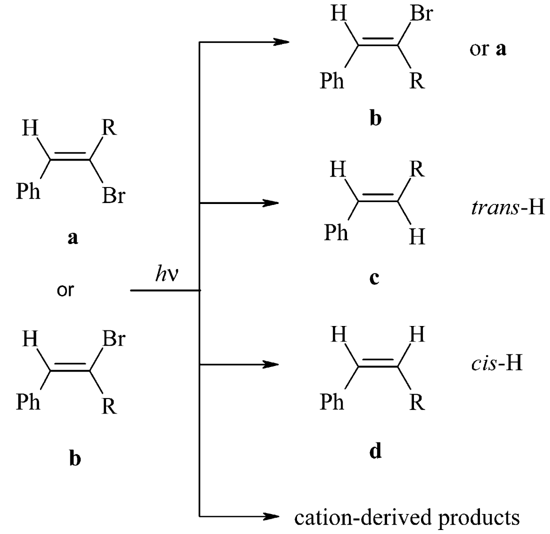
	1	**2**	**3**	**4**	**5**	**6**
R =	CH_3	F	C≡N	C(H)=O	C≡CH	$CH=CH_2$

Because of the discrepancy between the computational results obtained using post-HF[12,14] and DFT[13,14] methods for the structures of vinyl radicals with unsaturated α-substituents, the structures of the series $H_2C=C^{\cdot}–R$ with R = C≡N, C(H)=O, C≡CH and $CH=CH_2$ are subjected to a theoretical study and computed using the high-level QCISD(T)/6-311+G(d,p)//QCISD/6-311+G(d,p) approach.

Results and Discussion

Photochemistry

The photoreactions of the styryl bromides **1**–**6** typically yield *E*/*Z* isomerization, homolysis and heterolysis products, as depicted in Scheme 2. The points of focus in this study are the reductive dehalogenation products **c** and **d**, as they stem from an intermediate vinyl radical. This has been shown by the independent thermal generation of such species by reaction of vinyl halides with tri-*n*-butyltin hydride and azobis(isobutyronitrile) as an initiator.[16–18] The intermediate radical reacts with the solvent by transfer of a hydrogen atom. For the *Z*-bromides **1a**–**6a**, the *trans*-H products **1c**–**6c** are the result of vinyl radical trapping with retention, while the formation of the *cis*-H products **1d**–**6d** has occurred with inversion at the radical center. The opposite is true for the *E*-isomers **b**.



Scheme 2.

The vinyl cation-derived products include dehydrohalogenation and nucleophilic substitution products, sometimes after 1,2-rearrangement across the C=C double bond. Also hydride and halide shifts occur, typical of carbocation chemistry.[19]

Under oxygen-deficient conditions, the products **c** and **d** constitute the total of vinyl radical-derived products formed upon irradiation of the vinyl bromides under study.[20] The rates of *cis*-H and *trans*-H product formation have to be and are determined at low conversion of starting material to ensure that *E*/*Z* isomerization of substrates **a** and **b** or products **c** and **d** does not influence the yields of radical-derived products. The ratio of *cis*-H to *trans*-H product formation is k_d/k_c, or equivalently Φ_d/Φ_c, in terms of quantum yields. In the remainder of this paper, when referring to inversion (retention), the product obtained after inversion (retention) at the radical center of the intermediate is meant. This implies that k_d/k_c equals the ratio of inverted to retained product for *Z*-vinyl halides **a**, while the reciprocal value k_c/k_d corresponds to the same ratio for the *E*-isomers **b**.

α-CH_3- and α-F-Substituted Vinyl Radicals

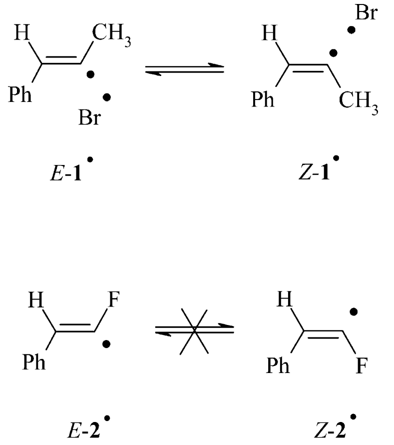
Irradiations of the α-methylstyrene bromides **1**, and the α-fluorostyrene bromides **2** in methanol yield vinyl radical-derived products. Homolysis is a minor reaction pathway for **1**,[17] but is effectively the only bond rupture process observed for **2**.[21] In Table 1 the quantum yields of formation of the two reductively dehalogenated isomers **c** and **d** and their ratio observed in the irradiation of the *E*- and *Z*-isomers of **1** and **2** are summarized.

Photohomolysis of the carbon halogen bond in the *Z*-isomer **1a** and the *E*-isomer **1b** gives nearly the same product composition (Table 1, entries 1 and 2). These results are similar to those of thermal experiments,[22,23] and are in agreement with a rapid *E*/*Z* equilibration of the bent β-phenyl-methylvinyl radicals *E*-$\mathbf{1}^{\cdot}$ and *Z*-$\mathbf{1}^{\cdot}$ (Scheme 3), which is faster than scavenging by the solvent. The slight deviation

Table 1. Quantum yields of formation ($10^2\Phi$) of the reductive dehalogenation products **c** and **d** and their ratios upon irradiation (λ_{exc} = 248 nm) of **1a**, **1b**, **2a**, and **2b** in methanol.

	Φ_c ($\times 10^2$)	Φ_d ($\times 10^2$)	Φ_d/Φ_c
1a	9.7	4.1	0.42
1b	9.7	3.4	0.35
2a	2.7	0	∞
2b	0	3.8	0

in stereoconvergence corresponds to a preference for inversion. This observation implies that non-complete equilibrium-establishment prior to scavenging can be excluded, because in that case the product compositions should reflect a bias for retention of configuration. Radical pair formation, however, can explain incomplete stereoconvergence. If the rate of radical pair diffusion is slow or comparable to that of scavenging by solvent, inversion of configuration will be favoured over retention. This is due to steric shielding of the incoming scavenger by the halogen atom. The preponderance of **1c** over **1d** is due to two factors, (a) the hydrogen atom transfer from the solvent methanol to **1**$^{\bullet}$ is a highly exothermic process,[24] and (b) the rates of hydrogen atom transfer from the small H-donor methanol to the two isomeric radicals are about equal. This implies[25] that the product ratio is determined by the equilibrium constant K for inversion between the *trans*- and the *cis*-vinyl radical *E*-**1**$^{\bullet}$ and *Z*-**1**$^{\bullet}$, which will be less than unity, leading to a ratio of >1:1 of **1c** vs. **1d**.



Scheme 3.

The reductive dehalogenation of the *E* and *Z* isomeric α-fluoro-substituted compounds **2a** and **2b** occurs with complete retention of configuration (Table 1, entries 3 and 4). Despite the possible involvement of initial radical pairs, not even a trace of inversion product is observed, which means that the radical itself does not invert. The α-fluoro vinyl radicals **2**$^{\bullet}$ (Scheme 3) thus are configurationally stable, bent species. This conclusion is in accordance with theoretical predictions[13,26] and with the results found for thermally generated α-fluorovinyl radicals.[13,27]

α-CN-Substituted Vinyl Radicals

Upon irradiation in methanol, the α-bromocinnamonitrile stereoisomers **3a** and **3b** show nearly stereoconvergence in their formation of **3c** and **3d**, with a slight bias for inversion as was the case for **1a** and **1b**. (See data in Table 2). The similar **3d/3c** ratios observed starting from **3a** or **3b** are compatible with a linear **3**$^{\bullet}$ as well as with rapidly equilibrating bent **3**$^{\bullet}$ s. To determine the structure of the α-cyanovinyl radical **3**$^{\bullet}$, **3b** was irradiated in methanol at five different temperatures over a 40 °C temperature range.

Table 2. Relative ratios of reductive dehalogenation ($k_d/k_c = k_{cis\text{-H}}/k_{trans\text{-H}}$) of compounds **3a** and **3b** upon irradiation (λ_{exc} = 254 nm) in methanol at various temperatures.

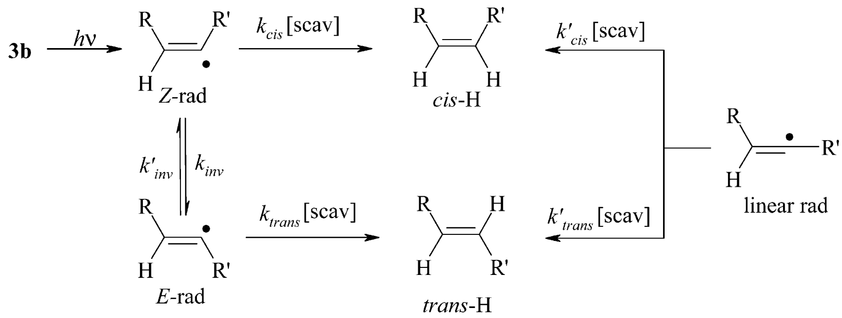
Substrate	T [K]	265	270	283	297	306
3a		1.30		1.50		1.83
3b		1.15	1.22	1.35	1.52	1.58

Analysis of *cis*- to *trans*-H product ratios as a function of temperature can distinguish between rapidly inverting bent and linear vinyl radicals (Scheme 4).

From this Scheme, which was first proposed by Singer[4a,22] and elaborated by Metzger and Blumenstein,[10] the following kinetic expressions for the ratio of *cis*- to *trans*-H formation can be deduced. For the bent radical (the left part of the Scheme) Equation (1) is valid, when starting with **3b** from which the *Z*-radical is photogenerated.

$$\frac{k_{cis\text{-H}}}{k_{trans\text{-H}}} = \frac{k'_{\text{inv}} \bullet k_{cis}}{k_{\text{inv}} \bullet k_{trans}} + \frac{k_{cis} \bullet [\text{scav}]}{k_{\text{inv}}} \qquad (1)$$

In a borderline case, valid here, inversion is fast relative to scavenging (Curtin–Hammett conditions), i.e. the inver-



Scheme 4.

sion barrier is low. Equation (1) is reduced to Equation (2) because $k_{cis}[\text{scav}] << k_{\text{inv}}$.

$$\frac{k_{cis\text{-H}}}{k_{trans\text{-H}}} = K_{Z\text{-rad}/E\text{-rad}} \; \frac{k_{cis}}{k_{trans}} \tag{2}$$

$K_{Z\text{-rad}/E\text{-rad}}$ is the equilibrium constant for the bent radicals, $k'_{\text{inv}}/k_{\text{inv}}$, and is expected to be less than unity.

For a linear radical, Scheme 4 yields [Equation (3)].

$$\frac{k_{cis\text{-H}}}{k_{trans\text{-H}}} = \frac{k'_{cis}}{k'_{trans}} \tag{3}$$

The scavenging reaction constants, k and k', are – a priori – not the same for an interconverting bent radical and a linear radical, because of the different angle of approach of the scavenger.[28]

$\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{-}(trans\text{-H})}$ is negative because *cis*-scavenging is less hindered than *trans*-scavenging. Therefore, if the logarithm of the $k_{cis\text{-H}}/k_{trans\text{-H}}$ ratio[29] is plotted against $1/T$, a linear radical will give a straight line with a positive slope. This follows from Equation (4), applying Eyring TS theory and expressing relative rates in terms of enthalpy and entropy differences.

$$\log \frac{\dfrac{k_{cis\text{-H}}}{T}}{\dfrac{k_{trans\text{-H}}}{T}} = \log \frac{k'_{cis}}{k'_{trans}} = -\frac{\Delta\Delta H^{\ddagger}_{(cis\text{-H})-(trans\text{-H})}}{R}\frac{1}{T} + \frac{\Delta\Delta S^{\ddagger}_{(cis\text{-H})-(trans\text{-H})}}{R} \tag{4}$$

For a bent radical a different equation is obtained [(i.e. Equation (5)], due to the presence of the equilibrium constant $K_{Z\text{-rad}/E\text{-rad}}$ in Equation (2).

$$\log \frac{\dfrac{k_{cis\text{-H}}}{T}}{\dfrac{k_{trans\text{-H}}}{T}} = \log K_{Z\text{-rad}/E\text{-rad}} \; \frac{k_{cis}}{k_{trans}} = -\frac{\Delta\Delta H^{\ddagger}_{(cis\text{-H})-(trans\text{-H})} + \Delta\Delta H^{0}_{(Z\text{-rad})-(E\text{-rad})}}{R}\frac{1}{T} + \frac{\Delta\Delta S^{\ddagger}_{(cis\text{-H})-(trans\text{-H})} + \Delta\Delta S^{0}_{(Z\text{-}rad)-(E\text{-rad})}}{R} \tag{5}$$

$\Delta\Delta H^{0}_{(Z\text{-rad})\text{–}(E\text{-rad})}$ is positive, because the *E*-radical is more stable than the *Z*-radical, and its value opposes the negative $\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{-}(trans\text{-H})}$-value. The difference is expected to be larger, the bulkier the scavenger. If $\Delta\Delta H^{0}_{\text{rad}}$ predominates, a negative slope will be found in the plot, and the radical is unambiguously established to be bent. A more qualitative consideration of such results leads to the same conclusion: when the thermodynamically favoured product is formed (relatively) less at elevated temperatures, a pre-equilibrium must be operative. When $\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{–}(trans\text{-H})}$ is larger than $\Delta\Delta H^{0}_{(Z\text{-rad})\text{–}(E\text{-rad})}$, however, a positive slope will be found. In that case it is impossible to discriminate between the bent and the linear species. If a reactive, small radical scavenger is used, $\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{–}(trans\text{-H})}$ is reduced to a minimum[30] and is expected to be less than $\Delta\Delta H^{0}_{(Z\text{-rad})\text{–}(E\text{-rad})}$, which relieves the indistinguishability of the two situations.

The *cis*-H to *trans*-H product ratios from **3b** were calculated from the measured rates of formation of the two isomeric products at the five different temperatures.[29] Also, the **3a** isomer was irradiated at three different temperatures to corroborate the results found for **3b**. In Table 2 the k_d/k_c ratios (which are equal to $k_{cis\text{-H}}/k_{trans\text{-H}}$) for compounds **3a** and **3b** at the various temperatures used are reported. When log ($k_{cis\text{-H}}/k_{trans\text{-H}}$) is plotted against $1/T$, for both **3a** and **3b** a straight line with a negative slope is found (Figure 1), with a correlation coefficient exceeding 0.990.

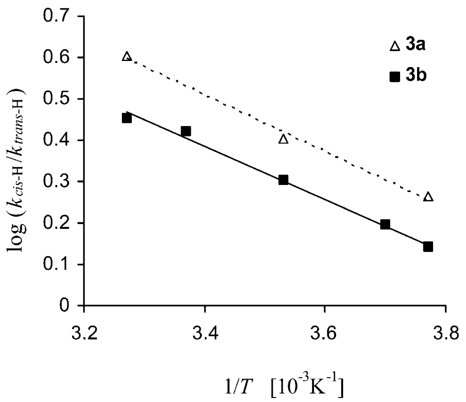
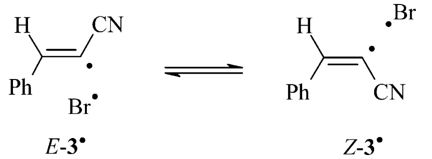


Figure 1. Plot of the log of the relative rates of formation of *cis*- to *trans*-olefin in the irradiations of **3a** and **3b** vs. $1/T$.

If **3a** and **3b** were to yield the same product-forming intermediate upon homolysis, the lines in Figure 1 would be coincident. This is clearly not the case: the *cis*-H/*trans*-H ratio is higher for **3a** than that for **3b** at a given temperature, but the lines are nearly parallel. Initial radical pair formation, which hinders attack at the initially formed radical, favouring inversion products slightly, can account for the non-coincidence. The same argument applied to the incomplete stereoconvergence in the case of α-methyl analogues **1a** and **1b**.

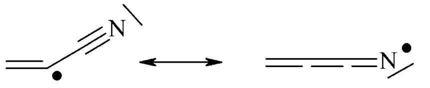
Figure 1 clearly shows that both lines have a negative slope, which amounts to $[\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{-}(trans\text{-H})} + \Delta\Delta H^{0}_{(Z\text{-rad})\text{–}(E\text{-rad})}]/R$, as can be seen from Equation 5. For **3a** and **3b** the values of the slopes are the same, and equal –1.3 kcal/mol. The difference in enthalpy of formation of the *cis* and the *trans*-radical thus exceeds the value of $\Delta\Delta H^{\ddagger}_{(cis\text{-H})\text{–}(trans\text{-H})}$ in methanol, by 1.3 kcal/mol. The overall negative slope establishes unambiguously that the intermediate β-phenyl-α-cyanovinyl radical **3·** is a rapidly inverting bent species (Scheme 5).



Scheme 5.

Metzger and Blumenstein have shown that the related β-cyclohexyl-α-cyanovinyl radical is a rapidly inverting bent species at high temperatures.[10] They stated that at room temperature, the radical might be linear because it may have a lower enthalpy than the bent vinyl radical, which is outweighed at higher temperatures by the higher entropy content of the bent species. Although such an argument is valid for the parent α-cyanovinyl radical $H_2C=C^{\cdot}–CN$, which is symmetrical when linear, this is not the case for the molecules under consideration because they have no symmetry.[31] Recently, however, flash photolysis of acrylonitrile has shown that the parent cyanovinyl radical is bent at room temperature.[32] We have now shown that also **3**$^{\cdot}$ is nonlinear at room temperature.

In an α-cyanovinyl radical, the cyano group is capable of delocalizing the single electron. The resonance contributor, however, is not very stabilizing, because the single electron is situated on an sp-hybridized electronegative nitrogen.



Apparently, resonance stabilization, which is at maximum for a π-type (sp-hybridized) vinyl radical, is counteracted by a destabilizing effect, which imposes a bent structure. Qualitatively, the non-linearity of the α-cyanovinyl radical is explained best by the model postulated by Dewar and Bingham:[33] α-substituents with low-lying π-electrons tend to destabilize a π-type radical and therefore to decrease the C=C–R angle. Apparently, the subtle opposing effects nearly cancel each other in **3**$^{\cdot}$, rendering the energy surface for bending shallow and the inversion barrier low.

α-C(H)=O, α-C≡CH, and α-CH=CH$_2$ Vinyl Radicals

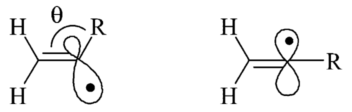
The method to produce stereoisomeric vinyl radicals under mild conditions by photolysis of vinyl halides did not work well for compounds **4**–**6**. Irradiation of the aldehyde-substituted **4a** in methanol gives a complex mixture of photoproducts (see ref.[16]), with the reductive dehalogenation products **4c/d** as minor components. This makes it difficult to obtain kinetic data. When **4a** is irradiated in diethyl ether only reductive dehalogenation occurs, next to *E*/*Z* isomerization. Remarkably, only the retention product **4c** is formed. This selectivity may be the result of scavenging a configurationally stable σ-type vinyl radical with retention or stereoselective scavenging of a linear intermediate leading to the *trans*-product.

To establish which case prevails, the *E*-isomer **4b** was synthesized by triplet-sensitized irradiation of **4a**. The *E*-isomer is not very stable and tends to reisomerize to **4a** thermally. Upon irradiation of **4b** in diethyl ether, eventually a trace of the reductive dehalogenation product **4c** is observed. The other radical product, **4d**, however, is not formed. It is questionable whether **4c** is produced from the vinyl bromide isomer **4b** or **4a**, as the latter was already present in considerable amounts (20%) by the time reductive dehalogenation became detectable. It may be that the only photoproduct of **4b** is the *Z*-isomer **4a** and that the latter undergoes photohomolysis, as described above, exclusively with retention to **4c**.

Irradiations of the acetylene-substituted **5a** and ethenyl-substituted **6a** in methanol yielded no reductive dehalogenation products. Instead, merely cation-derived products and *E*/*Z*-isomerization products are formed.[34,18]

Quantum Chemical Calculations

The parent vinyl radicals **3**, **4**, **5** and **6** with the unsaturated α-substituents depicted in Scheme 6 were subjected to a theoretical study. The structures were first optimized at the MP2/6-311+G(d,p) level followed by a frequency calculation to assure the nature of the stationary point. The structures were subsequently optimized at the QCISD-level, using the 6-311+G(d,p) basis set and single point energies were calculated at the QCISD(T)-level with the same basis set.[35] The optimized MP2 and QCISD structures are very similar, but preliminary B3LYP calculations showed a strong tendency to straighten the vinyl radical towards the linear π-type (vide infra). The angles of bending at the radical center (*θ*), the relative energies and the natures of the stationary points are summarized in Table 3. The calculations predict that for the substituents with a double bond, C(H)=O and $CH=CH_2$, the π-type structures **π4** and **π6** are energetically favored over the σ-type radicals. In order to effect allylic delocalization of the single electron, the π-substituent has to rotate out of the plane, and becomes perpendicular to the vinyl π-system. The imaginary frequency of the transition structure **σ6** rotates the α-$CH=CH_2$ out of this plane, and leads to **π6**.



Bent	Linear	R
σ3	**π3**	C≡N
σ4	**π4**	C(H)=O
σ5	**π5**	C≡CH
σ6	**π6**	$CH=CH_2$

Scheme 6.

Table 3. Results of quantum chemical calculations of the parent vinyl radicals **3**, **4**, **5** and **6** at the QCISD(T)/6-311+G(d,p)//QCISD/6-311+G(d,p) level.

	Substituent	Stationary point	Angle θ	Energy [kcal/mol][a]
σ3	C≡N	minimum	144.0	0
π3	C≡N	transition state	180	1.82
σ4	C(H)=O	minimum	130.8	0
π4	C(H)=O	minimum	180	–2.88
σ5	C≡CH	minimum	149.0	0
π5	C≡CH	transition state	180	1.23
σ6	$CH=CH_2$	transition state	136.6	0
π6	$CH=CH_2$	minimum	180	–7.83

[a] relative energy, with the σ-type radical set to 0 each time.

Upon photohomolysis of the vinyl bromide bond in either **4a** or **4b**, the α-C(H)=O-substituted vinyl radical will initially have the local minimum structure **σ4**. Since we only find radical product **4c** and not **4d** as a photoproduct of **4a**, it could be that scavenging of the vinyl radical in structure **σ4** is more rapid than its isomerization to the linear structure **π4**. At the MP2/6-311+G(d,p) level the barrier for this isomerization in vacuo is 1.43 kcal/mol. Solvent reorganization effects will significantly increase the entropic barrier.

For the vinyl radicals bearing an α-C≡N and an α-C≡CH group the bent structures **σ3** and **σ5** are favored over the linear ones, although the energy differences are small. The linear structures are in fact the transition structures for inversion, as their one imaginary frequency corresponds to the θ-angle bending coordinate. The activation barrier for inversion in the gas phase is equal to the energy difference between the linear and the bent structures, and is thus quite small. This flat potential energy surface along the vinyl bending coordinate implies that in solution these radicals will rapidly invert, with an activation barrier that is largely determined by the barrier associated with solvent reorganization. The triple bond substituents can participate in the electron delocalization while maintaining overlap with the vinyl moiety. This means that the structures of the bent and the linear species are alike. This contrasts with the vinyl radicals with the double bond substituents, in which the two π-systems are perpendicular in the linear species, but coplanar in the bent structure.

Our results for the α-cyanovinyl radical **3** are in line with other post-HF results[12,14] and disagree with earlier DFT calculations[13,14] which predict the linear structure to be more stable. We found that with the B3LYP/6-311+G(d,p) approach radicals **3** and **6** are both bent, but with very small deviations from linearity (167° and 178°) and negligibly small activation barriers ($<<0.1$ kcal/mol). Guerra has found that the stability of π-delocalized radicals is overestimated compared to that of σ-localized ones by the currently used density functionals.[36] This overestimation is probably the reason why Galli, Mencarelli, and co-workers[13] find the linear structure of **3** to be the more stable one using BLYP/6-31G(d,p).

The β-phenyl-α-cyano radical **3**$^{\cdot}$, which we experimentally determined to be bent and rapidly inverting, was also subjected to a theoretical study, using MP2/6-311+G(d,p). The bent radical with the cyano *trans* to the phenyl ring, at an angle of 135.5° was found to be the global minimum (Figure 2). The *cis* isomer, with an angle of 139.0°, is 0.85 kcal/mol higher in energy.

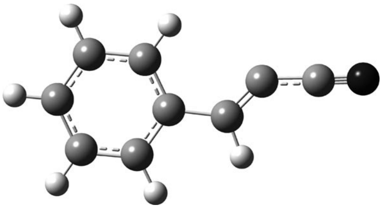


Figure 2. MP2/6-311+G(d,p)-optimized structure of the *trans*-β-phenyl-α-cyanovinyl radical **3**$^{\cdot}$.

Conclusions

Photolysis of *E*/*Z* isomeric vinyl bromides is found to be a convenient method to produce stereoisomeric vinyl radicals, under mild reaction conditions. The results of thermal experiments for the β-phenyl-α-methyl vinyl radical, which indicate a rapidly equilibrating bent species, are perfectly reproduced, if initial radical pair formation is taken into account. The α-fluorovinyl radical is proven to be a stable σ-radical.

Photolysis of *E* and *Z* α-cyanovinyl bromides, in combination with kinetic monitoring, has demonstrated that the β-phenyl-α-cyanovinyl radical is not linear but a rapidly inverting bent species. The experimental observation is supported by quantum chemical computations.

The method applied here is rather easy to generalize, but for some substituents adjustments in reaction conditions are necessary to get an appreciable yield of vinyl radicals. Care must be taken in studying the π- vs. σ-vinyl radical structure question by theoretical calculations, as the outcome is rather sensitive to the methodology.

Experimental Section

Irradiations: Products studies were carried out at λ_{exc} = 248 nm in a cuvette set up, with a Hanovia 977 B0010 high pressure Xenon lamp and an Oriel Grating monochromator model 77250. Triplet-sensitized irradiations were carried out in acetone at λ_{exc} = 313 nm using a Hanau TQ-81 high-pressure mercury arc and a filter solution consisting of 0.025 M potassium biphthalate, 1.0 M $NiSO_4$, and 0.25 M $CoSO_4$. The isothermal irradiations at various temperatures were performed at λ_{exc} = 254 nm with a Hanau TNN-15/32 low pressure mercury lamp. The lamp is separated from the solution, by immersing it in a tube with double quartz walls, separated by vacuum, filled with water. The tube is submerged in the cylindrical pyrex reaction vessel. The temperature of the reaction vessel is kept constant by submerging it in a dewar flask filled with water at a set temperature. All photochemical experiments were carried out under argon atmosphere.

Methanol (Rathburn Chemicals) and ether (p.a. quality, Baker) were used as supplied after checking for UV impurities. All substrates used in the photochemical experiments were 98+% purity (GC), except for **4b** (90%), which reisomerized to **4a**.

The solutions were about 10–15 mM in the pyrex reaction vessel and about 2–5 mM in the cuvette set-up (optically dense). An approximately equimolar amount of *n*-decane was used as an internal standard. The irradiations were carried out in triplicate. The quantum yields were calculated from the kinetic data obtained in the irradiations by using least-squares treatment and the intensity of light at the wavelength used. The values of the quantum yields reported are average values; the error (i.e., deviation from the mean) is typically 5%. The intensity of the light employed was determined by using a chemical actinometer: Actino Chromo 1R (248/334) from Photon Technology International. Each reaction constant k_c, k_d and quantum yield Φ_c, Φ_d was determined by using the least-squares method on at least seven samples taken at different times. All samples were taken within the first 4% of conversion of the starting materials. Typical correlation coefficients are in the range 0.94–0.99.

Analyses: Products were identified using gas chromatography and GC-MS of samples, coinjecting the alleged products with the product mixture. GC analyses were carried out with a Packard model 433 gas chromatograph, fitted with a CP-SIL 19 CB column (30 m, Ø = 0.32 mm), and hydrogen as a carrier gas. Preparative GC was performed using a Varian 920 Aerograph, fitted with a column (6 m, Ø = 8 mm) filled with 20% SE-30 on Chromosorb WAW, using hydrogen as the carrier gas. For the kinetic analyses, an automatic GC was used, from the HP 6890 Series, equipped with a CP-Sil-5B column (25 m, Ø = 0.25 mm).

^{1}H-, ^{19}F and noise decoupled ^{13}C-spectra were recorded on a Jeol JNM FX-200, a Bruker WM 300 or Bruker MSL 400, using $CDCl_3$ as a solvent and TMS (^{1}H), CF_3COOH (^{19}F) or $CDCl_3$ (^{13}C) as a reference. UV spectra were recorded on a Varian DMS 200 spectrophotometer, with methanol as a solvent. The low resolution mass spectra were recorded on a GC-MS set-up, consisting of a Hewlett–Packard model 438A gas chromatograph, fitted with a CP-SIL 5 CB column (25 m, Ø = 0.25) using helium as a carrier gas, coupled with a Finnigan Mat ITD 700 mass spectrometer. The high resolution mass spectra were recorded on a Finnigan Mat 900 mass spectrometer.

Reactants and Products: (*Z*)- and **(*E*)-2-bromo-1-phenylpropene** (**1a**, **1b**) were synthesized in a 40:60 ratio from α-methylcinnamic acid and NBS using a modified Hunsdiecker reaction.[37] The *E*- and *Z*-isomers were separated using column chromatography (silica/petroleum ether, boiling range 40–60 °C) in >98% purity. Their spectroscopic characterizations are reported in ref.[17].

Photoproduct **(*E*)-1-phenylpropene** (**1c**) is commercially available and **(*Z*)-1-phenylpropene** (**1d**) was prepared from **1c** by irradiation in acetone using light of λ_{exc} = 313 nm.[17]

(*Z*)-1-Bromo-1-fluoro-2-phenylethene (2a) and (*E*)-1-Bromo-1-fluoro-2-phenylethene (2b): To a solution of 13 g of triphenylphosphane in 125 mL freshly distilled, dry dichloromethane, 6.8 g tribromofluoromethane was added. Subsequently, in 15 min 2.6 g of benzaldehyde was added, and the solution was stirred for 7 h under nitrogen atmosphere. The reaction mixture was purified by silica column chromatography using hexane as the eluent to yield a 5:4 *E*/*Z*-mixture in a 0.4 g (15%) yield. The isomers were separated to an isomeric purity over 98% by preparative GC.

2a:[38] ^{1}H NMR: δ = 6.70 (d, 1 H, $^{3}J_{HF}$ = 15.2 Hz), 7.27 ppm (m, 5 H). UV: λ_{exc} = 245 nm ($\varepsilon = 1.1\times10^{4}$). MS: *m*/*z* (rel. int.) = 202 (100), 200 (90), 121 (70), 101 (55); high resolution MS: *m*/*z* = 199.9625 (calcd. 199.9637).

2b:[38] ^{1}H NMR: δ = 5.78 (d, 1 H, $^{3}J_{HF}$ = 32.6 Hz), 7.28 ppm (m, 5 H). UV: λ_{max} = 252 nm ($\varepsilon = 2.9\times10^{4}$). MS: *m*/*z* (rel. int.) = 202 (100), 200 (90), 121 (70), 101 (55); high resolution MS: *m*/*z* = 199.9623 (calcd. 199.9637).

The products **(*E*)-1-fluoro-2-phenylethene** (**2c**) and **(*Z*)-1-fluoro-2-phenylethene** (**2d**) were synthesized according to published procedures.[39]

2c: ^{1}H NMR: δ = 6.38 (dd, 1 H, $^{3}J_{HF}$ = 19.4 Hz, $^{3}J_{HH}$ = 11.4 Hz), 7.15 (dd, 1 H, $^{3}J_{HF}$ = 83.3 Hz, $^{3}J_{HH}$ = 11.4 Hz), 7.35 ppm (m, 5 H). ^{19}F NMR: δ = –53.9 ppm (dd, 1 H, $^{3}J_{HF}(\alpha)$ = 83.3 Hz, $^{3}J_{HF}(\beta)$ = 19.4 Hz). MS: *m*/*z* (rel. int.) = 122 (100), 121 (45), 101 (40), 96 (50); high resolution MS: *m*/*z* = 122.0553 (calcd. 122.0523).

2d: ^{1}H NMR: δ = 5.60 (dd, 1 H, $^{3}J_{HF}$ = 44.9 Hz, $^{3}J_{HH}$ = 5.4 Hz), 6.65 (dd, 1 H, $^{3}J_{HF}$ = 81.5 Hz, $^{3}J_{HH}$ = 5.4 Hz), 7.35 ppm (m, 5 H). ^{19}F NMR: δ = –46.2 ppm [dd, 1 H, $^{3}J_{HF}(\alpha)$ = 81.5 Hz, $^{3}J_{HF}(\beta)$ = 44.9 Hz]. MS: *m*/*z* (rel. int.) = 122 (100), 121 (45), 101 (35), 96 (45).

(*Z*)- (3a) and (*E*)-1-Bromo-1-cyano-2-phenylethene (3b): To a chilled (0 °C) solution of 5.0 g of cinnamonitrile in 100 mL tetrachloromethane, 12 g of bromine was added. The solution was stirred for 1 d at room temperature, and the excess bromine and solvent removed. The oily residue was dissolved in 40 mL of dry toluene, and 3.6 g triethylamine was added, after which the products crystallized. The solution was filtered and the precipitate washed with toluene. After evaporation of the solvent, the crude product (yield 88%) was purified into the separate isomers by silica column chromatography using a mixture of diethyl ether and petroleum ether (1:1) as an eluent.

3a: ^{1}H NMR: δ = 7.46 (m, 3 H), 7.75 ppm (m, 3 H). ^{13}C NMR: δ = 86.4, 128.3, 129.4, 130.8, 132.0, 145.0 ppm. UV: λ_{max} = 283 nm ($\varepsilon = 1.7\times10^{4}$), λ_{max} = 213 nm ($\varepsilon = 6.2\times10^{3}$), λ_{max} = 204 nm ($\varepsilon = 8.1\times10^{3}$). MS: *m*/*z* (rel. int.) = 209 (46), 207 (48), 128 (100), 101 (45), 77 (45).

3b: ^{1}H NMR: δ = 7.44 (m, 3 H), 7.54 (s, 1 H), 7.67 ppm (m, 2 H). UV: λ_{max} = 290 nm ($\varepsilon = 1.4\times10^{4}$), λ_{max} = 222 nm ($\varepsilon = 7.3\times10^{3}$), λ_{max} = 203 nm ($\varepsilon = 6.0\times10^{3}$). MS: *m*/*z* (rel. int.) = 209 (42), 207 (44), 128 (100), 101 (38), 77 (37).

Product ***trans*-cinnamonitrile** (**3c**) is commercially available and contains some ***cis*-cinnamonitrile** (**3d**). This mixture was used as such for product identification.

(*Z*)-2-Bromo-3-phenylpropenal (**4a**) is commercially available (α-bromocinnamaldehyde) and is isomerized to give **(*E*)-2-bromo-3-phenylpropenal** (**4b**) by triplet-sensitation using λ_{exc} = 313 nm and acetone as a solvent. The *E*-isomer is separated and purified by silica column chromatography using petroleum ether as an eluent.

4b: ^{1}H NMR: δ = 7.40 (m, 6 H), 9.55 ppm (s, 1 H). MS: *m*/*z* (rel. int.) = 212 (31), 210 (33), 211 (56), 209 (56),131 (24), 103 (83) [100] 102, 77 (96).

The photoproduct **(*E*)-3-phenyl-2-propenal** (**4c**) is commercially available (***trans*-cinnamaldehyde**) and **(*Z*)-3-phenyl-2-propanal** (**4d**) was prepared from **4c** by irradiation in acetone using light of λ_{exc} = 313 nm.

4d: ^{1}H NMR: δ = 6.19 (q, 1 H), 7.5 (m, 6 H), 9.96 ppm (d, 1 H). MS: *m*/*z* (rel. int.) = 132 (38), 131 (100), 104 (42), 103 (60), 78 (67), 77 (47).

(*Z*)-3-Bromo-4-phenylbut-3-en-1-yn (**5a**) was synthesized using a modification of a reported procedure.[40] To a solution of 13.1 g $[Ph_3PCH_2Br]Br$ in 130 mL THF cooled to –78 °C, under nitrogen atmosphere, 3.4 g (1 equiv.) *t*BuOK in 70 mL THF was added. The solution was stirred for 30 min, after which 6.4 g of α-bromocinnamaldehyde in 50 mL of THF was added dropwise. The solution was kept at –78 °C, and stirred for another 30 min. Subsequently, the second portion of 3.4 g *t*BuOK in 70 mL of THF was added, and the solution was warmed up to room temperature and stirred overnight. The solution was filtered, and the precipitate washed with petroleum ether. After evaporation of the solvent, the brown solid was washed with 4 portions of 150 mL of petroleum ether. The brown, oily residue after solvent removal was purified by silica column chromatography with a mixture of ether in petroleum ether as eluent (yield 18%). ^{1}H NMR: δ = 3.24 (s, 1 H), 7.32 (m, 4 H), 7.64 (m, 2 H), 7.98 ppm (s, 1 H). ^{13}C NMR: δ = 79.1, 83.1, 99.0, 128.3, 129.1, 129.2, 134.4, 138.1, 192.9 ppm. UV: $\lambda_{\max}$ = 276 nm (ε = 3.4×10^4), $\lambda_{\max}$ = 204 nm (ε = 2.2×10^4). MS: *m/z* (rel. int.) = 208 (33), 206 (35), 127 (100), 77 (24).

(*Z*)-2-Bromo-1-phenyl-1,3-butadiene (6a): To a cooled solution (–40 °C) of 9 g [Ph_3PCH_3]I in THF, 14 mL of 1.6 M BuLi in hexanes was added, and the solution was stirred for 50 min. After dropwise addition of 4.5 g α-bromocinnamaldehyde in 30 mL THF, the solution was warmed to room temperature and stirred for an hour. The solution was filtered, and the precipitate washed with petroleum ether. After evaporation of the solvent, the brown solid was washed with 4 portions of 100 mL of petroleum ether. The brown, oily residue after solvent removal was purified in a 38% yield by silica column chromatography with a mixture of dichloromethane in petroleum ether as an eluent. The spectroscopic characterization of **6a** is reported in ref.[18]

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