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Steric Influence of *E*- or *Z*-Monosubstituted and Terminally Disubstituted Vinyl Groups in Matrix-Isolated Cyclopentane-1,3-diyl Triplet Diradicals as Probed by the Zero-Field EPR *D* Parameter

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The zero-field *D* parameter of the localized *E*, *Z*, and disubstituted vinyl cyclopentane-1,3-diyl triplet diradicals **V** was determined at 77 K in a 2-methyltetrahydrofuran (2-MTHF) matrix. Good linear correlations were obtained with the semiempirically (PM3; $r^2 = 0.991$, $n = 19$) and DFT (B3LYP; $r^2 = 0.998$, $n = 7$) calculated spin densities of the triplet diradicals. The *D* values for the disubstituted triplet diradicals **V** are generally larger than the corresponding monosubstituted ones and, thus, the former are less well-delocalized and thereby more poorly stabilized. For the *E*- and *Z*-diastereomeric pairs **V**, only marginal changes in the theoretical assessed spin densities as well as in the *D* values have been found. Steric effects operate and distort the conformation of the vinyl substituent in the triplet diradical **V**. This is adequately reproduced by theoretical calculations. For the diphenyl-substituted triplet diradical **Vl**, for example, they show a more or less planar alignment of the *E*-phenyl group and the allylic π system (torsion angle 12°) and thus optimal delocalization of spin, whereas the *Z*-phenyl group is twisted about 78° out of plane and therefore is not involved in the delocalization and stabilization of spin. This results in a slightly higher *D* value (0.0368 cm^{-1}), and the spin is delocalized less than in the monosubstituted *E*-**Vm** one (0.0357 cm^{-1}).

Introduction

Triplet diradicals are conveniently generated through photochemical deazetation of the corresponding azoalkanes **2**.[1,2] The resulting 1,3-cyclopentanediyl triplet diradicals persist in organic matrixes at 77 K, detectable by EPR spectroscopy, and characterized by the zero-field splitting (zfs) parameters *D* and *E*. Of these, *D* provides information on electronic effects in radicals.[2,3]

The *D* parameter may be described as a two-center dipolar interaction between the two radical sites, whose magnitude depends on the interspin distance d_{AB} and the spin densities ρ_A and ρ_B at the respective radical sites A and B (eq 1). The spin-density dependence of the *D*

$$D = \frac{3\mu_0 g^2 \mu_B{}^2}{16\pi}\left(\frac{\rho_a \rho_b}{d_{ab}{}^3}\right) \tag{1}$$

parameter was examined for a great variety of substituents at the *meta* and *para* positions of the phenyl group,[4] and recently an extensive set of *E*-configured vinyl substituents has been investigated.[5] Excellent correlations have been found between the *D* parameter of the triplet diradicals and experimentally assessed α-hyperfine coupling constants (α-hfc), as well as with spin-density calculations of the respective monoradicals. Hence, the *D* parameter is a reliable probe to evaluate the electronic substituent effects in cyclopentane-1,3-diyl triplet diradicals and infer from these the electronic stabilization in the corresponding monoradicals.

In this context, vinyl-substituted cyclopentane-1,3-diyl triplet diradicals have been employed to assess electronic substituent effects in allylic radicals.[5] Such triplet diradicals offer the opportunity to investigate the electronic effects of *E* and *Z* substitution in the vinyl group and from them infer valuable information on the delocalization and stabilization in the correspondingly substituted allylic monoradicals. As for the latter, the little that is known on this subject is contradictory: As an example, for the chloro derivative the *E*- and *Z*-monosubstituted and the disubstituted allylic radicals **A** all have the same α-hfc values (14.8 G), whereas for the methoxycarbonyl-substituted allylic radical, the *E* diastereomer (13.7 G) has a lower value than the *Z* one (14.3 G), and thus the former delocalizes the spin better.[6,7] Presumably, steric effects are at play for the *Z* isomer, which twist the vinyl

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[1] Borden, W. T. *Diradicals*; Plenum Press: New York, 1978.

[2] Dougherty, D. A. In *Kinetics and Spectroscopy of Carbenes and Diradicals*; Plenum Press: New York, 1990; pp 117−142.

[3] (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall: Englewood Cliffs, 1969. (b) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; Wiley: New York, 1994.

[4] Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *24*, 205−254.

[5] (a) Emmert, O. Dissertation, University of Würzburg, March 2000. (b) Adam, W.; Emmert, O. *J. Org. Chem.* **2000**, *65*, 4127−4130.

[6] (a) Sustmann, R.; Trill, H.; Brandes, D. *Chem. Ber.* **1977**, *110*, 245−254. (b) Sustmann, R.; Trill, H.; Vahrenholt, F.; Brandes, D. *Chem. Ber.* **1977**, *110*, 255−263.

[7] (a) Richerzhagen, T.; Svejda, P.; Volman, D. H. *J. Phys. Chem.* **1973**, *77*, 1819−1822. (b) Griller, D.; Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 758−759.

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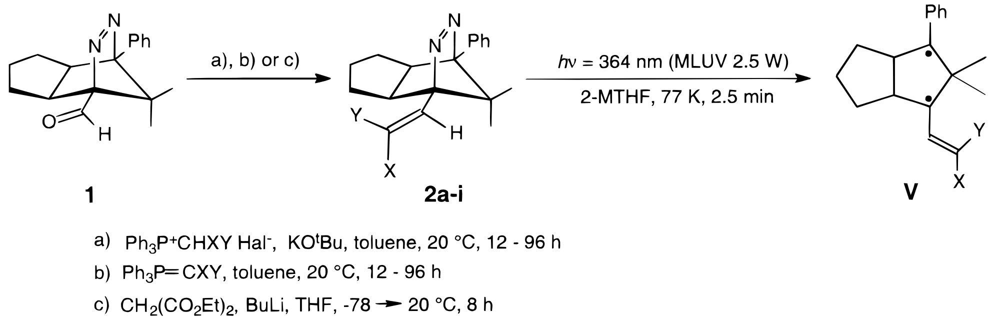
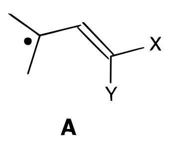
Scheme 1. Synthesis of the Azoalkane 2 and Generation of the Corresponding Vinyl-Substituted Cyclopentane-1,3-diyl Triplet Diradicals V[a]



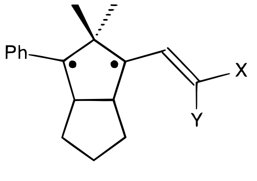
[a] (a) Ph$_3$P$^+$CHXY Hal$^-$, KO^{t}Bu, toluene, 20 °C, 12−96 h; (b) Ph$_3$P=CXY, toluene, 20 °C, 12−96 h; (c) CH$_2$(CO$_2$Et)$_2$, BuLi, THF, −78 → 20 °C, 8 h.

substituent out of planarity with the radical center and the electronic stabilization by spin delocalization is reduced. This would be expected for terminally disubstituted allylic radicals, but again the experimental data is inconsistent: For the dimethoxy-substituted derivative, indeed, the α-hfc constant is higher (14.97 G) than for the *E*,*Z*-monosubstituted (14.07 G) ones;[6] however, for the methyl, cyano, and ethoxycarbonyl cases the opposite is observed,[7] i.e., electronic stabilization overrides steric effects.

To assess quantitatively the importance of electronic stabilization versus deconjugation by steric effects, it was of interest to examine a series of *E*,*Z*-monosubstituted and terminally disubstituted vinyl derivatives of the cyclopentane-1,3-diyl triplet diradicals **V** and assess from the *D*-parameter data the effects in the allylic monoradical fragments **A**. Convenient and effective synthetic methodology (Wittig olefination[8]) has recently become available[9] for the preparation of the required azoalkanes with *E*- and *Z*-configured monosubstituted and terminally disubstituted vinyl groups. From such azoalkanes the corresponding triplet diradicals are readily generated photolytically in a low-temperature matrix, and the *D* parameter are measured by EPR spectroscopy. Herein, we report our results for the *E*- and *Z*-configured monosubstituted and disubstituted vinyl groups in the cyclopentane-1,3-diyl triplet diradicals **V**, which demonstrate that steric effects dominate.



A



V

Code	X	Y
Z-**a**	H	OMe
E-**a**	OMe	H
b	H	H
c	Me	Me
Z-**d**	H	SiMe$_3$
E-**d**	SiMe$_3$	H
E-**e**	Me	H
Z-**f**	H	I
E-**f**	I	H
Z-**g**	H	Br
E-**g**	Br	H
Z-**h**	H	Cl
E-**h**	Cl	H
i	CO$_2$Et	CO$_2$Et
Z-**j**	H	CO$_2$Et
E-**j**	CO$_2$Et	H
E-**k**	CN	H
l	Ph	Ph
E-**m**	Ph	H

Results

Synthesis. The required azoalkane precursors were synthesized according to literature procedures.[9] Wittig–Horner olefination of the azoalkane **1** with an excess of the appropriate phosphorane gave the azoalkane **2**, while Knoevenagel condensation of the malonate ester afforded the azoalkane **2i** (Scheme 1).

EPR Spectroscopy. The diradicals **V** were generated in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K by irradiation of the azoalkanes **2** (Scheme 1). All diradicals possess a greenish-yellow color and persist at 77 K, as established by the constant EPR signal intensities. The results of the EPR measurements for the *Z*- and the disubstituted triplet diradicals **V** are summarized in Table 1 and compared with the known *E*-substituted ones.[5] For convenience, the *D* values have been arranged in descending order, the methoxy one *E*-**Va** ($D = 0.0480$ cm^{-1}) has the largest and the monophenyl one *E*-**Vm** the smallest values. Except for the SiMe$_3$ substituent, the differences between the *E* and *Z* diastereomers are within the experimental error (±0.0001 cm^{-1}). Even for the Me$_3$Si-substituted isomers *E*-**Vd** ($D = 0.0451$ cm^{-1}) and *Z*-**Vd** ($D = 0.0460$ cm^{-1}), the difference is marginal. Mechanistically significant, the *D* values for the disubstituted triplet diradicals **V** are in general slightly higher, by 0.0006−0.0011 cm^{-1}, than the corresponding monosubstituted ones, as illustrated for the phenyl-substituted pair *E*-**Vm** ($D = 0.0357$ cm^{-1}) and **Vl** ($D = 0.0368$ cm^{-1}). Therefore, the disubstituted ones exhibit smaller spin-accepting properties than the monosubstituted ones. These electronic substituent effects of the vinyl group in the cyclopentane-1,3-diyl triplet diradicals shall now be

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(8) Wittig, G.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 1373−1383.

(9) Adam, W.; Emmert, O.; Heidenfelder, T. *J. Org. Chem.* **1999**, *64*, 3417−3421.

Table 1. Experimental Zero-Field *D* Values of the Matrix-Isolated *E*- and *Z*-Monosubstituted and Terminally Disubstituted Vinyl Triplet Diradicals V and Their Theoretical Spin Densities

diradical[a]	X	Y	$\|D/hc\|$ (cm^{-1})[b]	spin densities (ρ)[c]
Z-**Va**	H	OMe	0.0478	0.681
E-**Va**	OMe	H	0.0480	0.690
Vb	H	H	0.0473	0.630 (0.531)
Vc	Me	Me	0.0462	0.557 (0.516)
Z-**Vd**	H	$SiMe_3$	0.0460	0.583
E-**Vd**	$SiMe_3$	H	0.0451	0.531
E-**Ve**	Me	H	0.0456	0.523 (0.508)
Z-**Vf**	H	I	0.0449	0.530
E-**Vf**	I	H	0.0450	0.527
Z-**Vg**	H	Br	0.0446	0.509
E-**Vg**	Br	H	0.0446	0.506
Z-**Vh**	H	Cl	0.0438	0.448
E-**Vh**	Cl	H	0.0437	0.452
Vi	CO_2Et	CO_2Et	0.0421	0.375 (0.471)
Z-**Vj**	H	CO_2Et	0.0415	0.347
E-**Vj**	CO_2Et	H	0.0413	0.333 (0.463)
E-**Vk**	CN	H	0.0400	0.291
Vl	Ph	Ph	0.0368	0.150 (0.416)
E-**Vm**	Ph	H	0.0357	0.108 (0.398)

[a] The data for all *E* diastereomers have been taken from ref 5 and for the parent system from ref 9. [b] Experimental *D* values were obtained from the EPR spectra recorded in a 2-MTHF (2-methyltetrahydrofuran) matrix; error ± 0.0001 cm^{-1}. [c] Spin densities were calculated for the triplet diradicals **V** by the semiempirical PM3 AUHF method, implemented in the VAMP 6.1 program package (ref 10); in addition, the spin densities for the triplet diradicals **V** were calculated with the ab initio method B3LYP (values given in parentheses), as implemented in the Gaussian 98 program package (ref 11).

diagnosed in terms of spin-density calculations for the allyl-radical fragment **A** in the triplet diradicals **V**.

Discussion

Recently, we have shown that the experimental results for the *D* parameter of *E* vinyl-substituted triplet diradicals correlate well ($r^2 = 0.989$, $n = 16$) with the semiempirical spin densities of the corresponding allylic monoradicals.[5] When such analysis was attempted for the *Z* diastereomers and the disubstituted triplet diradicals **V** reported herein, a poor correspondence ($r^2 = 0.783$, $n = 8$) was found. With the possibility of steric effects in mind in the disubstituted allylic radicals, the semiempirical calculations were performed directly on the set of *E*- and *Z*-mono- and disubstituted vinyl triplet diradicals **V**. Indeed, the calculated spin densities at the allylic position in the diradicals **V** correlate well ($r^2 = 0.991$, $n = 19$) with the experimentally assessed *D* values (Figure 1).[10] This good agreement is corroborated by the excellent linear correlation ($r^2 = 0.998$, $n = 7$) of the disubstituted and the corresponding *E*-monosubstituted triplet diradicals **V**, performed on the DFT level (B3LYP 6−31 g*); these spin densities are given in parentheses in Table 1.[11]

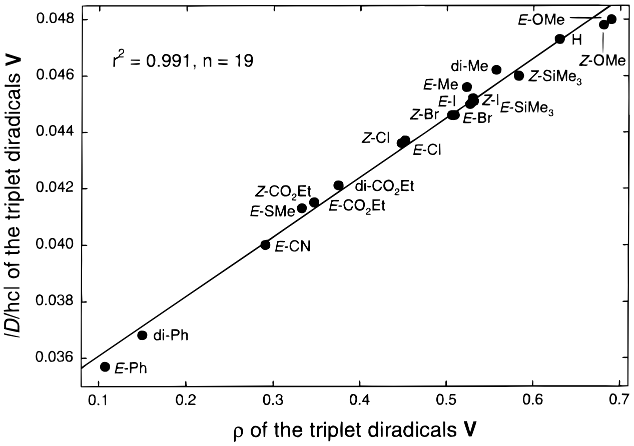

Figure 1. The *D* values for the *E*- and *Z*-monosubstituted and terminally disubstituted vinyl triplet diradicals **V** versus their semiempirically (PM3 AUHF) calculated spin densities.

Two remarkable points are evident in the correlation in Figure 1: First, the *D* values for the disubstituted triplet diradicals **V** are generally larger than the corresponding monosubstituted ones, e.g., the phenyl-substituted derivatives *E*-**Vm** ($D = 0.0357$ cm^{-1}) versus **Vl** ($D = 0.0368$ cm^{-1}); second, there is almost no difference between the *D* values of the *Z* and *E* diastereomers. Both effects are also evident in the theoretical spin densities! Since for the disubstituted derivatives the spin density at the allylic radical site is higher than for the corresponding monosubstituted ones, the former are less delocalized and stabilized. In contrast, for the *Z*- and *E*-diastereomeric pairs **V** only marginal changes in the theoretically assessed spin densities are found.

Unquestionably, steric effects operate, which distort the planar alignment of the vinyl substituent with the radical center in the triplet diradical **V**. These steric effects are not present in the allylic monoradical **A** (for a clear-cut case, compare the respective silyl-substituted triplet diradical *Z*-**Vd** and the allyl monoradical *Z*-**Ad**); consequently, a good correlation between the experimentally assessed *D* values, and the calculated spin densities are only achieved for the mono- and disubstituted triplet diradicals (Figure 1), if the spin density of the triplet species is computed.[12]

This steric hindrance is particularly well demonstrated in the calculated minimum-energy conformation for the phenyl substituent of the disubstituted triplet diradical **Vl** and the monosubstituted diastereomer compared to *E*-**Vm** (Figure 2). For the latter, the vinyl group is in plane with the allylic radical site and, more significant, also the *E*-phenyl substituent is more or less in the same plane (torsion angle ca. 8°). This signifies good alignment and, thus, effective delocalization in the vinylic π system. Essentially the same conformation applies also to the *E*-phenyl group in the disubstituted derivative **Vl** (torsion angle 12°). In contrast, the *Z*-phenyl group is twisted about 78° out of plane and is not involved in the delocalization and stabilization of the spin. Furthermore,

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(10) Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T.; Sauer, W.; Beck, B.; Hutter, M.; Gedeck, P. VAMP 6.1, University of Erlangen-Nürnberg, 1996.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, Q.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.

(12) (a) Adam, W.; Barneveld van, C.; Gerke, J.-S.; Klärner, F. G. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2723−2728. (b) Adam, W.; Barneveld van, C. *J. Am. Chem. Soc.* **1999**, *121*, 10820−10827.

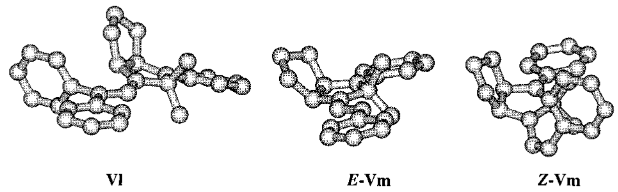

Figure 2. Calculated minimum-energy conformations (B3LYP 6-31g*) for the phenyl-disubstituted triplet diradical **Vl** and the *E* and *Z* diastereomers **Vm**; for better clarity, the hydrogen atoms are not shown.

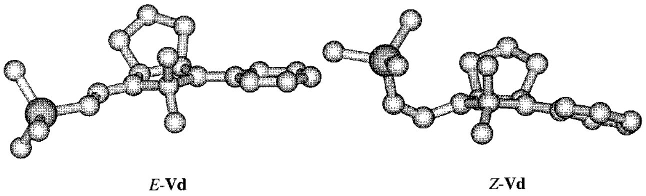

Figure 3. Calculated minimum-energy conformations (B3LYP 6-31g*) for the trimethylsilyl-substituted triplet diradicals *E*-**Vd** and *Z*-**Vd**; for better clarity the hydrogen atoms are not shown.

the two phenyl groups in **Vl** force the cyclopentane ring of the triplet diradical species slightly out of planarity. For comparison, we have also calculated the *Z* diastereomer *Z*-**Vm**, although no experimental *D* value is available. It also possesses a nonplanar conformation of the phenyl substituent with the vinyl group (Figure 2); in fact, it is essentially as strongly twisted out of conjugation as the *Z*-phenyl group in the disubstituted derivative **Vl**. For the latter, the *D* value is slightly higher (0.0368 cm^{-1}), and it delocalizes the spin less than the monosubstituted *E*-**Vm** one (0.0357 cm^{-1}). Consequently, the *gem* disubstitution of the two phenyl groups at the vinyl terminal causes mutual out-of-plane twisting. Thus, in the minimum-energy conformation, the *Z*-phenyl causes the *E*-phenyl group in the disubstituted derivative **Vl** to be less effectively conjugated, as corroborated by the dihedral angle of ca. 12°. These steric interactions are also observed for the other disubstituted triplet diradicals in Table 1, but they are more pronounced for the phenyl pair.

Also in the diastereomeric *E* and *Z* pairs steric effects may operate, as illustrated in the Me_3Si-substituted pair *E*-**Vd** (0.0451 cm^{-1}) and *Z*-**Vd** (0.0460 cm^{-1}). Expectedly, the *Z* diastereomer (Figure 3) is significantly more twisted out of conjugation than the *E* one.

However, for the other *E*,*Z* pairs examined herein (Table 1), the *D* values of the triplet diradicals are the same within the experimental error, i.e., within ±0.0001 cm^{-1}. Therefore, it is not surprising that in the sterically less-encumbered allylic radicals **A**, the influence of *E* and *Z* substitution is nominal, as evidenced by the nearly equal α-hfc values for the *E*-CN (13.10 G) and *Z*-CN (13.25 G) diastereomers, and the same values (14.8 G) for the *E*-Cl and *Z*-Cl pair.[6a]

We conclude from the present *D*-parameter data (Table 1) for the cyclopentane-1,3-diyl triplet diradicals **V** with sterically ineffective vinyl substituents that neither the substitution pattern (*E* versus *Z* monosubstitution) nor the degree of substitution (mono- versus disubstitution) change the spin density and the efficacy of the spin delocalization significantly (the *D* values are within the experimental error). Indeed, the spin delocalization is determined by the electronic nature and quality of the substituent to stabilize the unpaired electron. However, when sterically demanding groups as the phenyl and trimethylsilyl substituents are located at the terminal end of the vinyl functionality, steric effects become important and the *D* values are slightly higher (more spin localization at the ring-contained radical center and thereby less stabilization) than expected from the electronic influence of the substituent. Even then, the magnitude of the steric interaction is surprisingly small (ca. 3% in the *D* values). In the parent triplet diradical **Vb**, the vinyl group is only slightly twisted out of planar alignment (dihedral angle between the vinyl π bond and the plane of the cyclopentane-1,3-diyl ring is ca. 8°) due to the steric repulsion with the annelated cyclopentane ring and the *gem*-dimethyl group of the cyclopentane-1,3-diyl system. The terminal substituent (only the *Z*-configured one) on the vinyl functionality changes the extent of this *inherent twisting* through enhanced steric repulsions; however, the potential energy well for out-of-plane twisting (deconjugation) for a π group is quite shallow, and the influence of the spin density and, thus, the *D* parameter is small. To corroborate these small changes in the spin density, the complete cyclopentane-1,3-diyl triplet diradical **V** must be computed, because these steric effects are specific for this structural entity and do not apply in the allylic monoradicals **A**.

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Supporting Information Available: Synthetic details and characteristic spectral data of the azoalkanes **2** are presented. This material is available free of charge in the Internet under http//:www.pubs.acs.org.

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