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Rotational Barrier in 1-Cyano-1-methoxyallyl Radical: A Contribution to the Problem of Capto-Dative Radical Stabilization

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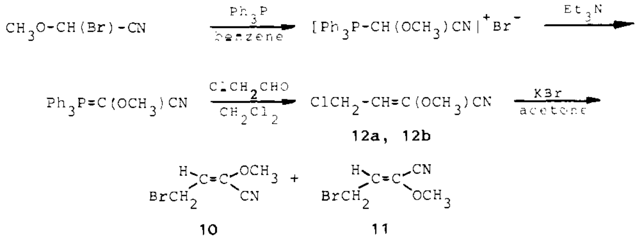
Abstract: The combined action of a donor and acceptor substituent on the rotational barriers in *syn*-1-cyano-*anti*-1-methoxyallyl radical and *anti*-1-cyano-*syn*-1-methoxyallyl radical ($E_a = 6.0 \pm 0.4$ and 6.1 ± 0.6 kcal/mol, respectively) has been evaluated via ESR spectroscopy. Comparison of these values with the rotational barriers in 1-deuterioallyl radical (15.7 ± 1.0 kcal/mol), 1-cyanoallyl radicals (10.2 ± 0.9 kcal/mol), and 1-methoxyallyl radicals (14.5 ± 1.1 kcal/mol) (mean values for syn/anti and anti/syn isomerization) shows a lowering of the barrier which slightly (2.9 ± 2.0 kcal/mol) exceeds the additivity of the individual substituent effects. This is more than in the case of two like substituents where no additive substituent effects are observed. As these substituent effects reflect a thermodynamic contribution to the radical stabilization, a special capto-dative radical stabilization may be deduced for this system.

It is commonly accepted that organic free radicals are stabilized by electron donors as well as electron acceptors (see refs 1–7 and references cited therein). However, the magnitude of the stabilization of free radicals by donor or acceptor substitution is still of great interest, because quantitative measures of radical stabilization strongly depend on the chemical system used in the particular investigations.[4,8]

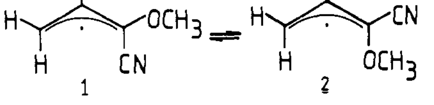
A few years ago, Viehe and co-workers[9] postulated that the combined action of donor and acceptor substituents on a radical center should lead to an enhanced stabilization compared to donor/donor or acceptor/acceptor substitution. A special effect of this kind, remaining unnoticed however, had first been suggested by theoretical arguments in 1952.[10] Effects which seem also in accord with this scheme were observed experimentally from time to time and termed "merostabilization",[11,12] "push–pull stabilization",[13] or "donor–acceptor stabilization".[14] In this paper we will use the term "capto-dative (cd) substituent effect", as introduced by Viehe.[9] Theoretical investigations[15] predict a synergetic effect of capto-dative radical substitution, i.e., the stabilization should exceed the sum of the individual stabilization effects of the substituents. Other calculations[8] failed to predict a significant synergetic behavior.

In this connection it is essential to remember the different meaning of radical stabilization (i.e., thermodynamical lowering of the radical ground-state energy) and persistency,[16] which describes kinetic stabilization (i.e., increase of the radical lifetime under defined conditions). In most cases radical self-termination reactions in solution (recombination, disproportionation) are highly exothermic and the termination rates approach the diffusion-controlled limit. In the absence of steric hindrance the thermodynamical stabilization of the radical resulting from introduction of an electron-delocalizing substituent does not affect the termination rates to an extent overriding the diffusion control by the solvent.[17] Recently, we have shown[18] that this idea still holds in the case of capto-dative substitution: the decay of sterically unperturbed capto-dative substituted methyl radicals in solution occurs with diffusion-controlled reaction rates via dimerization. Despite the large amount of experimental work about capto-dative substituted radicals, only few investigations[12,19,20] are accessible on measures of capto-dative stabilization.

Scheme I



We therefore carried out an investigation concerning the evaluation of a quantitative number of the capto-dative radical stabilization from the ESR spectroscopical determination of the rotational barrier in the isomeric 1-cyano-1-methoxyallyl radical **1** and **2**.



Rotational barriers in delocalized radicals provide good measures for radical stabilization[21-24] because the barrier is predom-

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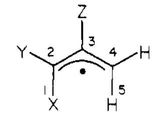
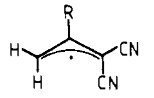
Table I. ESR Parameters for Allyl Radicals

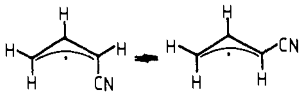
	T, °C[a]	g factor[b]	hyperfine couplings, mT[c] a_1	a_2	a_3	a_4	a_5	ref
1	−80	2.00318	0.211	0.208	0.338	1.093	1.006	*d*
	−51	2.00317	0.209	0.207	0.341	1.097	1.009	
	−21	2.00321	0.208	0.194	0.351	1.089	1.009	
	+4	2.00322	0.209	0.192	0.353	1.082	1.005	
2	−81	2.00316	0.173	0.242	0.311	1.071	1.030	*d*
	−51	2.00315	0.170	0.243	0.314	1.072	1.033	
	−21	2.00314	0.166	0.243	0.316	1.077	1.034	
	+4	2.00316	0.163	0.243	0.324	1.076	1.034	
3a	−33		0.160	0.195	0.320	1.216	1.130	*f*
3b	−40		0.154	0.197		1.149	1.082	*f*
4	−38	2.00385	0.189	1.503	0.378	1.315	1.242	*e, f*
5	−40	2.00277	1.418	0.220	0.379	1.305	1.220	*e, f*
6	−68	2.00293	0.084	0.084	0.233	1.491	1.435	*d, g*
	+109		0.058	0.075	0.263	1.445	1.390	*d*
7	+32	2.00305	0.073	0.103	0.250	1.469	1.407	*d*
	+117	2.00302	0.070	0.099	0.267	1.452	1.392	
8	−60	2.00296	0.143	1.417	0.315	1.364	1.318	*d, h*
	+72		0.129		0.332			*d*
9	−60	2.00304	1.398	0.112	0.362	1.311	1.307	*d, h*
	+72			0.129	0.380			*d*
13	−60	2.00255	1.392	1.481	0.406	1.481	1.392	i

[a] ±2 °C. [b] ±0.00002. [c] ±0.002 mT. [d] This work. [e] Reference 17c. [f] Reference 21b. [g] Reference 33. [h] Reference 21c. [i] Reference 24; Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* 1963, *39*, 2147.

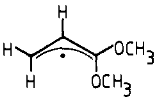
inantly determined by the loss in delocalization energy in the transition state of the rotation. The isomerization **1** ⇌ **2** was selected because the direct observation of the capto-dative substituted radicals avoids complications due to ground-state effects on the radical precursors and polar and steric influences on the transition state of formation of the radicals should be the same. The extent of capto-dative stabilization is obtained by comparison with the known rotational barriers in the cyano-substituted allyl radicals **3b**,[21a] **4**, and **5**,[21b] and the alkoxy-substituted allyl radicals **6**–**9**. Attempts to determine the rotational barriers in the latter radicals are also subject to this study.



3a, R = H
3b, R = C(CH$_3$)$_3$



4 5



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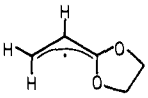

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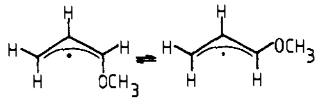

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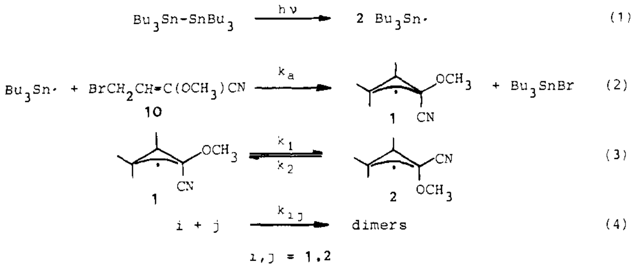
Results

Barrier to Isomerization of 1 and 2. 4-Bromo-2-methoxy-*cis*-crotononitrile (**10**) and 4-bromo-2-methoxy-*trans*-crotononitrile (**11**), synthesized according to Scheme I, were used as precursors in the stereospecifical generation of radicals **1** and **2**, respectively. Compounds **10** and **11** produce the desired radicals in a clean manner and yield the highest ESR signal intensity of the precursors tested in this study.

Separation of the cis/trans isomer mixture was achieved by preparative GLC at the stage of the chloro compounds **12**. Isomeric purity of the bromo compounds **10** and **11** was 90–93% by ^{1}H NMR.

Scheme II



Radicals **1** and **2** were generated stereospecifically from **10** and **11**, respectively, by reaction with photolytically generated tri-*n*-butylstannyl radicals (Scheme II, eq 1 and 2). By photolyzing solutions composed of 20 vol% of **10** (respectively **11**), 20 vol% hexa-*n*-butylditin, and 60 vol% tetrahydrofuran in the ESR cavity, we were able to record well-resolved ESR spectra of radicals **1** and **2** in the temperature range of −105 to +60 °C. Table I lists the coupling constants and g-values at selected temperatures. Figure 1 displays the ESR spectra that were obtained at −60 °C. Both spectra are superpositions of the individual spectra of **1** and **2**, in a ratio different from the isomeric composition of the starting material and therefore indicate interconversion of the two cd allyl radicals at this temperature.

Scheme II displays the relevant reactions which occur during photolysis. Justification for this reaction scheme was obtained from a product analysis. The only products formed in the termination of the allylic radicals **1** and **2** are a set of dimerization products, tetrasubstituted 1,5-hexadienes. No cross-coupling products with tributylstannyl radicals could be found. Compounds related to radicals formed by addition of tributylstannyl radicals to the starting cd olefins were not detected.

Reactions 1–4 are described kinetically by the steady-state eq 5 and 6 in which $I = k_a[\mathbf{10}][\mathrm{Bu_3Sn}\cdot]$ stands for the formation of

$$d[\mathbf{1}]/dt = I - 2k[\mathbf{1}]^2 - 2k_t[\mathbf{1}][\mathbf{2}] - k_1[\mathbf{1}] + k_2[\mathbf{2}] \qquad (5)$$

$$d[\mathbf{2}]/dt = k_1[\mathbf{1}] - k_2[\mathbf{2}] - 2k_t[\mathbf{2}]^2 - 2k_t[\mathbf{1}][\mathbf{2}] \qquad (6)$$

radical **1** according to eq 2. Furthermore, the termination rate constants k_{ij} are replaced by the common termination rate constant $2k_t$, because the dimerization of the capto-dative allyl radical can

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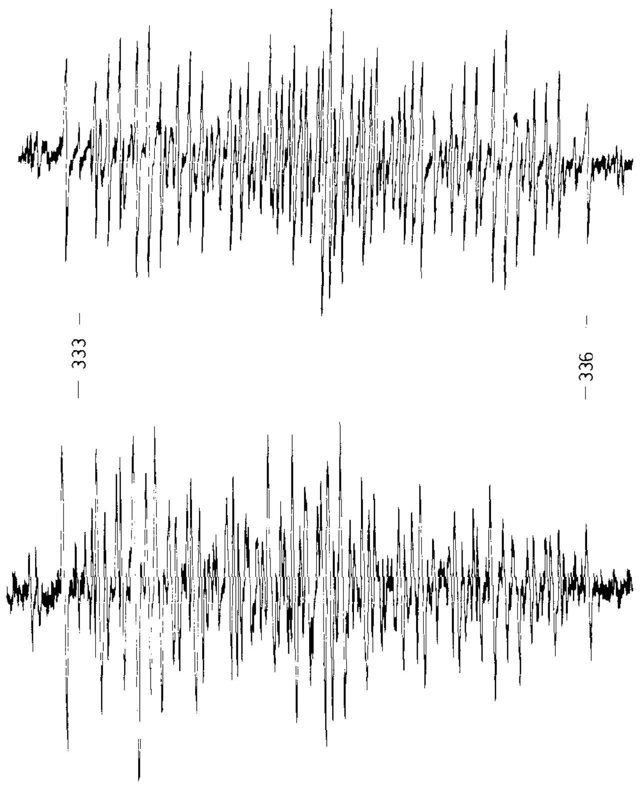

Figure 1. ESR spectra of *syn*-1-cyano-*anti*-1-methoxyallyl radical (**1**) (bottom) and *anti*-1-cyano-*syn*-1-methoxyallyl radical (**2**), (top) generated from 4-bromo-2-methoxy-*cis*-crotononitrile (**10**) and 4-bromo-2-methoxy-*trans*-crotononitrile (**11**) by reaction with tri-*n*-butylstannyl radicals at −60 °C. Field markers in mT.

safely be assumed to be diffusion controlled as is the case for the closely related 1-cyanoallyl radicals.[17c,25] Evaluation with respect to the concentration ratio [**1**]/[**2**] leads to[21b]

$$[\mathbf{1}]/[\mathbf{2}] - 1/K = (2k_t I)^{1/2}/k_1 \qquad (7)$$

where $K = k_1/k_2 = [\mathbf{2}]_{eq}/[\mathbf{1}]_{eq}$ is the equilibrium constant for isomerization of radicals **1** and **2**. Insertion of the Arrhenius equations $k_1 = A_1 \exp(-E_a{}^1/RT)$ and $2k_t = A_t \exp(-E_a{}^t/RT)$ yields eq 8 as the final equation. The activation energy $E_a{}^1$ for

$$\log \{([\mathbf{1}]/[\mathbf{2}] - 1/K)/I^{1/2}\} = \log (A_t{}^{1/2}/A_1) + (E_a{}^1 - E_a{}^t/2)/2.3RT \qquad (8)$$

isomerization **1** → **2** can be determined from the ratio of [**1**]/[**2**] as a function of temperature and from a consideration of the temperature dependence of the other quantities in eq 8. The barrier $E_a{}^2$ for isomerization **2** → **1**, assumed not to be identical with $E_a{}^1$, can be obtained by inserting **11** and exchanging **1** and **2** in the derivation of eq 8.

In the determination of $E_a{}^1$ and $E_a{}^2$ two approximations are made: First, the temperature dependence of the unknown rate constant k_a for bromine abstraction by tributylstannyl radicals is approximated by the relation

$$\log k'_a = (9500 \pm 500) - (2300 \pm 500)/2.3RT \qquad (9)$$

which leads to rate constants in the range 5×10^7 to 5×10^8 M^{-1} s^{-1}. The activation parameters of the latter Arrhenius equation are deduced from the experimental activation parameters and rate constants for bromine abstraction from benzyl and allyl compounds by triethylsilyl radicals[26] and the reasonable assumption of 10–50 times lower rate constants for bromine abstraction by tributylstannyl radicals compared to triethylsilyl radicals.[27] The steady-state radical concentration of $Bu_3Sn\cdot$ can be estimated arbitrarily because only the temperature dependence and not the absolute value of I influences the value of E_a. The term I was then calculated for each temperature where [**1**]/[**2**] was measured. The second approximation is the replacement of the activation energy $E_a{}^t$ for recombination of the cd allyl radicals by the activation energy E_η for the solvent viscosity η. Several investigations[17,18,28] with regard to the diffusion control of radical-decay reactions in solution have shown that the activation energy $E_a{}^t$ for recombination is governed by the activation energy E_η for the viscosity. In the case of diffusion-controlled radical-termination reactions $E_a{}^t$ and E_η do not differ more than 0.5 kcal/mol. For our solution E_η was determined as 2.63 ± 0.07 kcal/mol.

The isomerization **1** → **2** was followed by ESR spectroscopy in the temperature range of −80 to +36 °C, where either **1** or **2** was the starting radical. The concentration ratios [**1**]/[**2**] were obtained by comparing the intensity ratio of the experimental spectra with computer-simulated superimposed spectra of given ratios. A small correction was made for the isomeric composition of the radical precursors. At +36 °C the ratio [**1**]/[**2**] was found to be 0.56 ± 0.13, independent of using **10**, **11**, or a 1:1 mixture of **10** and **11** as starting substrate This indicates the attainment of the thermodynamical equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$ at this temperature. From the equilibrium constant $K = 1.79 \pm 0.40$ at +36 °C a free enthalpy difference of $\Delta G° = -0.36 \pm 0.13$ kcal/mol in favor of **2** was determined. Using this value, the equilibrium constant K was calculated at the temperatures of the ESR measurements.

Starting from 4-bromo-2-methoxy-*cis*-crotononitrile (**10**) as radical precursor, least-squares analysis of the plot $\log \{([\mathbf{1}]/[\mathbf{2}] - 1/K)/I^{1/2}\}$ vs. $1/T$ yields an activation energy for isomerization **1** → **2** of $E_a{}^1 = 6.0 \pm 0.4$ kcal/mol.

Starting from radical **2**, the equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$ is reached earlier, i.e., at lower temperatures, as **2** is the thermodynamically more stable radical. In this case, the variation of the ratio [**2**]/[**1**] in the experimentally accessible temperature range proves to be too small to evaluate $E_a{}^2$ with sufficient accuracy. Therefore, we calculated the barrier $E_a{}^2$ by combining the experimental values of $E_a{}^1$ and $\Delta G°$ via $E_a{}^2 = E_a{}^1 - \Delta G° - T\Delta S°$, which follows from inserting the difference of the activation energies into the Gibbs–Helmholtz equation. An estimate of the unknown reaction entropy $\Delta S°$ was achieved using model compounds for the radicals.[29] The reaction entropies $\Delta S° = 3.8$ e.u. and $\Delta S° = 0.98$ e.u. for cis/trans isomerization of crotononitrile[30] and 1-methoxypropene,[31] respectively, give $\Delta S° = 2.8$ e.u. for the entropy difference of *cis*- and *trans*-2-methoxycrotononitrile, the parent molecules of radicals **1** and **2**. Assuming a somewhat lower entropy difference in the case of the radicals[29] (restricted rotation about the CH_3—CH= bond does no longer exist), we take 1.5 e.u. as a reasonable estimate for the upper limit of $\Delta S°$. In the given temperature range the term $T\Delta S°$ then amounts to 0.3 (±0.2) kcal/mol, leading to an activation energy for isomerization **2** → **1** of $E_a{}^2 = 6.1 \pm 0.6$ kcal/mol. The higher standard deviation accounts for the uncertainty in the entropy difference.

The given limits of the activation energies are the standard values from the least-squares analysis. Taking into consideration the above approximations, we conclude that the error limits might be somewhat higher but should not exceed ±1 kcal/mol (twice the standard error). For instance, calculation of the barrier $E_a{}^1$, taking the radical generation term I independent of temperature, showed that the influence of the term I is very low and lies well within the error limits.

Barrier to Isomerization of 8 and 9. Alkoxy groups are regarded as low to moderate radical stabilizing substituents. However,

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(25) A measurement of the decay of radical **1** at −40 °C by time-resolved ESR spectroscopy gave a bimolecular rate constant in the order of 8×10^8 M^{-1} s^{-1}, confirming the diffusion control of the radical decay.

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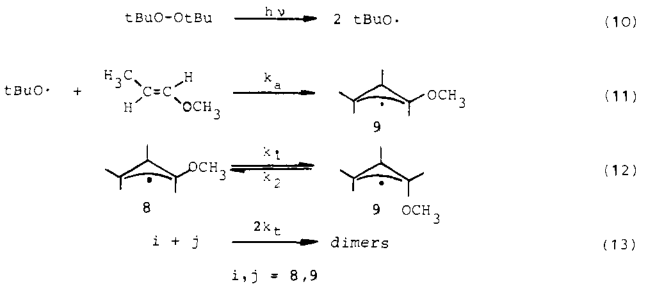
Scheme III



quantitative measures of their stabilizing influence scatter significantly.[2-8] For allylic systems, values of the stabilization energy range from 2.4 to 4.3 kcal/mol.[32] In order to establish the extent of stabilization in our capto-dative substituted allyl radicals **1** and **2** by comparison with the stabilizing influence of the isolated substitutents, we have investigated the syn/anti isomerization of the 1-methoxyallyl radicals **8** and **9**.

anti-1-Methoxyallyl radical **9** was generated stereospecifically from *trans*-1-methoxypropene (methyl propenyl ether) by attack with photolytically generated *tert*-butoxyl radicals in trichlorofluoromethane solution. The ESR spectrum recorded at −106 °C displays the superposition of the hyperfine patterns of radical **9**[21c] (see Table I for ESR parameters) together with weaker signals of a secondary radical, compatible with the radical deriving from hydrogen abstraction at the ether methyl group.

Surprisingly, photolysis of di-*tert*-butyl peroxide (DTBP) in the presence of *cis*-1-methoxypropene in $CFCl_3$ at −106 °C only produces a very weak ESR spectrum of the expected *syn*-1-methoxyallyl radical **8**[21c] (see Table I for ESR parameters), but a far more intense spectrum of a radical with coupling constants 2.56 mT (3 H), 2.425 mT (1 H), and 2.250 mT (1 H) (g = 2.00293). The coupling constants are incompatible with a radical deriving from hydrogen abstraction at the ether methyl group but can reasonably be assigned to the 1-methoxy-1-*tert*-butoxy-2-propyl radical, deriving from addition of *tert*-butoxyl radicals to the 1-position of 1-methoxypropene. The latter spectrum is not observed if radicals **8** and **9** are generated from allyl methyl ether.[21c]

As the predominant formation of the adduct radical in the case of *cis*-1-methoxypropene is observed up to +50 °C, we were only able to investigate the isomerization **8** ⇌ **9** starting from *trans*-1-methoxypropene, generating radical **9**. The ESR spectroscopical determination of the isomerization **9** ⇌ **8** was carried out by photolyzing a 25 vol% solution of *trans*-1-methoxypropene in DTBP in the temperature range +20 to +90 °C. Above + 40 °C, the hyperfine lines of the *syn*-1-methoxyallyl radical **8** could be observed.

With respect to the temperature dependence of the concentration ratio [**9**]/[**8**], derivation of the steady-state rate equations connected with Scheme III yields the same equation (eq 8) as in the case of radicals **1** and **2**. The equilibrium constant $K = [\mathbf{8}]_{eq}/[\mathbf{9}]_{eq}$ was obtained by simultaneous generation of radicals **8** and **9** during photolysis of a 1/1 (vol) mixture of methyl allyl ether and DTBP. Between +6 and +85 °C the ratio of the corresponding ESR signal intensity does not vary very much; K = 2.18 ± 0.24 (+6 °C), K = 1.97 ± 0.22 (+85 °C). Thus, the attainment of the thermodynamical equilibrium **9** ⇌ **8** at +85 °C can safely be assumed. This leads to a free reaction enthalpy for isomerization of $\Delta G°$ = −0.48 ± 0.10 kcal/mol. Neglecting the temperature dependence of the radical generation term I (corresponding to eq 11) and replacing the activation energy E_t for recombination by the activation energy E_η = 2.37 ± 0.06 kcal/mol for viscous flow of the solution, the least-squares analysis of the experimental intensity ratios [**9**]/[**8**] gives $E_a{}^1$ = 14.3 ± 1.4 kcal/mol for the anti/syn isomerization of radical **9**. The isomerization barrier **8** → **9** is estimated to 14.7 ± 1.5 kcal/mol, considering the enthalpy difference $\Delta G°$.

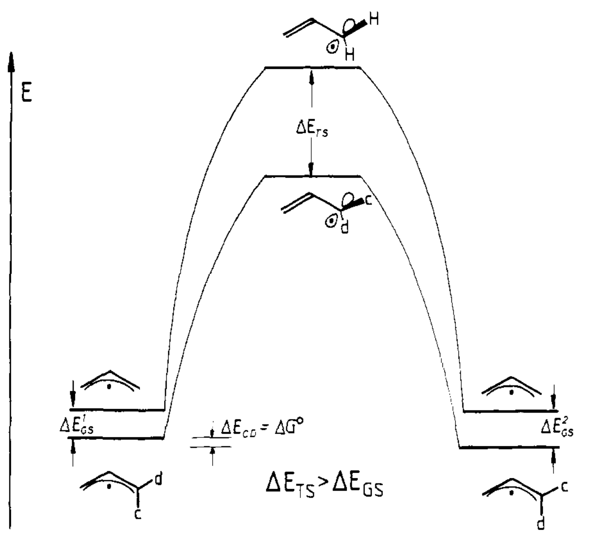


Figure 2. Stabilization of allylic radicals.

The low signal-to-noise ratio of the ESR spectra is responsible for the relatively high error limits of this activation barrier. Nevertheless, the low stabilization effect of the methoxy group (approximately 1.2 kcal/mol) on allylic radicals is clearly established by comparison with the rotational barrier of 15.7 kcal/mol in the 1-deuterioallyl radical.[24]

Barrier to Rotation in 6 and 7. Further insight into the mechanism of capto-dative radical substitution should be provided by comparison with the stabilization effects of symmetrical capto/capto and dative/dative disubstitution at the radical center.

Rotation in a symmetrically 1,1-disubstituted allyl radical leads to the identical radical. Therefore, ESR line shape analysis should be applicable to the dialkoxy-substituted radicals **6** and **7** if the *syn*- and *anti*-hydrogen atoms of the alkoxy groups show different hyperfine splittings in the ESR spectrum.

1,1-Dimethoxyallyl radicals **6** were generated in the temperature range −70 to +109 °C by photolyzing deoxygenated solutions of acrolein dimethyl acetal and DTBP in chlorobenzene (1/1/1 by volume). In the ESR spectrum of radical **6** the hfs couplings of the *syn*- and *anti*-methoxy hydrogens are found to be equivalent below −50 °C (see Table I), in agreement with literature data.[33] This equivalence is unlikely to be due to rapid rotation about the C^1–C^2 allylic bond but rather an indication for a specific preferential conformation of the two methoxy groups, leading to an accidental equivalence of the methyl couplings at low temperature. Above 0 °C, where rapid rotation about the CH_3O–C bonds is expected, the coupling constants of the methyl hydrogens are different by 0.023 mT. Up to 109 °C, the highest temperature which could be reached, no indication for selective line broadening in the ESR spectrum could be observed. With these values and assuming a "normal" A factor of 10^{13}, a *lower limit* of 12 kcal/mol for the rotational barrier in **6** is calculated, using the approximative relation $k = \pi\Delta a/\sqrt{2}$ for the difference of coupling constants and the rate constant for inversion at the coalescence temperature.[34]

A further approximation to the stabilization energy of geminal alkoxy groups was obtained from the ESR investigation of the 1-(ethylenedioxy)allyl radical **7**. During photolysis of a 1/1 mixture of 2-vinyl-1,3-dioxolane and DTBP at room temperature, an ESR spectrum of radical **7** was recorded, showing hyperfine splittings for *syn*- and *anti*-methylene groups different by 0.028 mT (see Table I). A complete ESR spectrum of radical **7** could be recorded up to +125 °C, parts of the spectrum up to +160 (±10) °C. As no significant line shape variations were observed

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(32) (a) Berson, J. A.; Walsh, Jr., E. J. *J. Am. Chem. Soc.* **1968**, *90*, 4731. (b) Kirmse, W.; Marowski, H. R.; *J. Chem. Soc., Chem. Commun.* **1977**, 122. (c) Alfassi, Z. B.; Golden, D. M. *Int. J. Chem. Kinet.* **1973**, *5*, 295.

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Table II. Rotational Barriers in Allyl Radicals (kcal/mol)

	radical	E_a	$\Delta G^\ddagger$	ref
13	$\mathrm{CH_2{=}CH{-}\dot{C}HD}$	15.7 ± 1.0		*a*
4	*syn*-$\mathrm{CH_2{=}CH{-}\dot{C}HCN}$	10.6 ± 1.3		*a, b*
5	*anti*-$\mathrm{CH_2{=}CH{-}\dot{C}HCN}$	9.8 ± 1.1		*a, b*
3b	$\mathrm{CH_2{=}C(C(CH_3)_3){-}\dot{C}(CN)_2}$	9.6 ± 0.3	9.0 ± 0.1	*c*
8	*syn*-$\mathrm{CH_2{=}CH{-}\dot{C}HOCH_3}$	14.7 ± 1.5		*d*
9	*anti*-$\mathrm{CH_2{=}CH{-}\dot{C}HOCH_3}$	14.3 ± 1.4		*d*
6	$\mathrm{CH_2{=}CH{-}\dot{C}(OCH_3)_2}$	>12		*d*
7	$\mathrm{CH_2{=}CH{-}\dot{C}(OCH_2)_2}$	>13.5		*d*
1	$\mathrm{CH_2{=}CH{-}\dot{C}(OCH_3)CN}$	6.0 ± 0.4		*d*
2	$\mathrm{CH_2{=}CH{-}\dot{C}(OCH_3)CN}$	6.1 ± 0.6		*d*
	syn-$\mathrm{CH_2{=}CH{-}\dot{C}HCH_3}$		14.3	*e*
	$\mathrm{CF_2{=}CH{-}\dot{C}F_2}$		7.2	*f*
	$\mathrm{CF_2{=}CF{-}\dot{C}F_2}$		6.1	*f*
	$\mathrm{CF_2{=}CCl{-}\dot{C}F_2}$		4.5	*f*

[a] Reference 24. [b] Reference 21b. [c] Reference 21a. [d] This work. [e] Gorton, P. J.; Walsh, R. *J. Chem. Soc., Chem. Commun.* 1972, 783. [f] Smart, B. E.; Krusic, P. J.; Meakin, P.; Bingham, R. C. *J. Am. Chem. Soc.* 1974, *96*, 7382.

at these temperatures, the rotational barrier about the C^1–C^2 allylic bond in **7** is estimated to *greater* than 13.5 kcal/mol.

Discussion

The hypothesis that the rotational barrier in an allylic radical is a good measure of the radical stabilizing effect of a substituent rests on the assumption which is shown pictorially in Figure 2. In the ground state of the substituted allylic radical the substituent is attached to a carbon atom at which the spin density is <1 (0.63 for the unsubstituted allyl radical).[35] Its influence, which should be proportional to the spin density, therefore should be smaller in the ground state than in the orthogonal transition state, where the spin density at the radical center is 1.0. Assuming the substituent stabilizes the radical, ΔE_{TS} is greater than ΔE_{GS} (see Figure 2) and the rotational barrier is lowered compared to the unsubstituted allyl radical **13**.

The experimental results shown in Table II lend support to this interpretation and furthermore disclose some interesting points. Cyano substitution reduces the rotational barrier of the unsubstituted allyl radical **13** from 15.7 ± 1.0 to 10.2 ± 0.9 kcal/mol (mean value from **4** and **5**), i.e., the radical stabilization energy of a cyano group is 5.5 ± 1.3 kcal/mol in this system. Introduction of a second cyano group has only a very small additional stabilizing effect (9.6 ± 0.3 kcal/mol for **3b**). There is no additivity in the substituent effects for two cyano groups. One methoxy group affects the stability of the allyl radical by approximately 1.2 ± 1.4 kcal/mol, as deduced from the barriers to rotation in **8** and **9**. The lower limits of the barriers for the dialkoxy-substituted radicals **6** and **7** suggest a stabilization energy smaller than 3 kcal/mol for two geminal alkoxy substituents, possibly again no additivity in substituent effects. Assuming the stabilizing effects of cyano and alkoxy substituents to be additive, a value of 9.0 ± 1.7 kcal/mol is expected[36] for the rotational barrier in the 1-cyano-1-methoxyallyl radicals **1** and **2**. This value is 2.9 ± 2.0 kcal/mol higher than the experimentally determined barrier of 6.0–6.1 (±1.0) kcal/mol. As the effect is slighlty more than additive (with regard to the given error limits), it is more than found for geminal c/c or d/d substitution.

How do our results compare with other investigations? Recently, Rüchardt and co-workers[20] studied the kinetics and the thermochemistry of decomposition of *meso*- and D,L-2,3-dimethoxy-2,3-diphenylsuccinonitrile, the dimers of the α-cyano-α-methoxybenzyl radical. They observed additivity of substituent effects and no synergetic increase. However, they are not able to exclude a small synergetic stabilization because of the uncertainties[37] in the thermodynamical estimates necessary.

The cis/trans isomerization of para-substituted tetraphenylethylenes[12a] and tetraphenylcyclopropanes,[12b] which are assumed to proceed via biradicals or biradicaloid transition states, leads to a small reduction in activation energies for capto-dative (cyano-methoxy) substituted systems. Unfortunately, the conclusions concerning the influence of capto-dative substitution are somewhat restricted because by these methods it is not possible to determine the barriers of isomerization for symmetrically c/c or d/d disubstituted compounds.

Cis/trans isomerization of substituted cyclopropanes[19a,38], shows markedly decreased activation barriers in the case of geminal capto-dative substitution. However, cyclopropanes are suspected not to be suited as well for this problem, because steric and/or polar influences on the ground and transition states may play an important role in the isomerizations.[37,39]

Conclusions

The rotational barriers in the isomeric capto-dative substituted 1-cyano-1-methoxyallyl radicals are markedly decreased compared to the corresponding capto and dative mono- and disubstituted radicals.

However, the determined "extra" stabilization may not exceed the additivity of the individual substituent effects very much. In many cases, however, multiple substitution of the same kind does not lead to an additive influence of the substituents,[40] so the ability of the substituents to interact additively in radicals might be termed already a special capto-dative substituent effect. This interpretation can be rationalized by MO descriptions[15] or by additional zwitterionic valence-bond resonance structures.[11,12]

Even though the energetic effects of capto-dative substitution in free radicals seem to be not very large, the additivity of substituent effects combined with a possible small synergetic contribution may influence the product distribution of reactions, where these radicals are intermediates. Certain reaction paths like hydrogen abstraction, disproportionation, or addition to double bonds may no longer be accessible, giving high yields of radical dimers as is observed experimentally.[9]

Experimental Section

ESR Measurements. The ESR measurements were performed using a Bruker ER-420 X-band spectrometer equipped with a variable temperature unit. Radicals were generated by UV irradiation of the solutions in sealed Suprasil quartz tubes (4-mm ϕ) with the light of a 1-kW Hg/Xe high-pressure lamp (Hanovia 977B-1). Most of the experimental equipment has been described elsewhere.[18,24] Temperatures were measured by means of a thermocouple placed at a distance a few millimeters outside the ESR cavity below the bottom of the sample tubes. Corrections for a temperature gradient and for heating due to irradiation were made by placing a small thermocouple (0.25-mm ϕ) inside the sample tube and monitoring the temperature of the solutions during irradiation as a function of the temperature of the nitrogen stream used for controlling the temperature.

THF was purified by distillation from $LiAlH_4$ under argon atmosphere and stored over molecular sieves. Hexa-*n*-butylditin[41] was distilled twice under argon atmosphere. DTBP (Peroxid-Chemie) was purified by filtering twice over neutral alumina (Woelm). Chlorobenzene was purified by distillation from P_2O_5 and passing over basic alumina prior to use.

The solutions used in the ESR measurements were degassed by three freeze-pump-thaw cycles.

The ESR hyperfine coupling constants were evaluated by simulation of the ESR spectra on a PDP-11/34 computer, on-line with the ESR spectrometer. The relative intensities of the interconverting radicals in the isomerization measurements were evaluated by comparing the experimental spectra with simulated superimposed ESR spectra of given relative weights. The comparison was done for adjacent line pairs throughout the whole spectra in order to correct for the variations of the signal intensity due to depletion of substrates and CIDEP effects. Each intensity ratio is the mean value of 12–25 measurements from at least

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(35) According to INDO calculations on a MNDO-optimized geometry. Details of calculations on this and other substituted allylic radicals will be published elsewhere.

(36) The given error limits of the derived values are calculated with consideration to the propagation of errors.

(37) Rüchardt, Ch., private communication.

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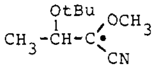
(41) We thank Prof. W. P. Neumann, University of Dortmund, for a gift of hexa-*n*-butylditin.

two independent recordings of the spectra. The values were corrected for the isomeric composition of the radical precursors.

As mentioned before, the mixture of 4-bromo-2-methoxycrotononitrile (**10** and **11**), hexa-*n*-butylditin, and THF was best suited for the generation of radicals **1** and **2**, respectively, with regard to the ESR signal intensity and the applicable temperatures. Attempts to generate radicals **1** and **2** by hydrogen abstraction from *cis*- or *trans*-2-methoxycrotononitrile were unsatisfactory, because the ESR signal intensity appeared to be too low, even at −90 °C. Additionally, at temperatures above +50 °C the ESR spectrum of a radical (a = 1.439 (1 H), 0.356 (1 N), 0.209 (3 H) mT; g = 2.00323, +122 °C) was observed, tentatively assigned to radical **14** formed by addition of *tert*-butoxyl radicals to the precursors. The abstraction of chlorine from the 4-chloro-2-methoxycrotononitriles **12a** and **12b** by photolytically generated triethylsilyl radicals produces a higher ESR signal intensity at low temperatures but also leads to the formation of an adduct radical (**15**) (a = 0.59 (1 H), 0.183 (3 H), 0.030 (2 H), 0.350 (1 N) mT; g = 2.00345, +35 °C) at higher temperatures.



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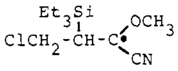

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Viscosity Measurements. Dynamic viscosities were determined with the aid of a micro-Ubbelohde viscosimeter (Schott). For all solutions, the temperature dependece of the dynamic viscosities is well described by the Andrade law with correlation coefficients >0.999.

Product Analyses. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian XL-200 and EM-360A spectrometers. Me_4Si was used as internal standard. Mass spectra (70 eV) were obtained by means of a Varian MAT 312/188 spectrometer connected with a Varian 3700 gas chromatograph equipped with a 70-m OV-101 glass capillary column. Infrared spectra were recorded on a Perkin-Elmer 397 instrument. GC analyses were performed on a Varian 3700 instrument and preparative GC separations on a Varian 940 Aerograph.

The photolyzed solutions of the isomerization measurements of radicals **1** and **2** were analyzed by GC on a 2-m aluminum column packed with 10% DEGS on Chromosorb G. After photolyzing a mixture of 20% 4-bromo-2-methoxycrotononitrile (**10** and **11**), 20% hexa-*n*-butylditin, and 60% THF (by volume) for 0.5 h six product peaks were found, accounting for 88–96 % of all new products. The relative intensities of these peaks varied depending on irradiation temperature and starting material (**10** and **11**). Assignment of the product peaks to the dimers of radicals **1** and **2** (dimethoxydicyanohexadienes) was confirmed by the mass spectra, which for all major product peaks showed a maximum m/e of 192, corresponding to the expected M$^+$ of the dimers. The 100% peak at m/e 96 is assigned to the 1-cyano-1-methoxyallyl cation. Additionally, the ^{1}H NMR spectra (C_6D_6) of the products, isolated by preparative GC on a 3-m DEGS column were well compatible with the structures of the different possible tetrasubstituted hexadienes.

2-Bromo-2-methoxyacetonitrile was synthesized in 54% yield by standard procedures[42,43] starting from formaldehyde: bp 43–46 °C (15 mbar); ^{1}H NMR (CCl_4) δ 3.6 (s, 3 H), 6.25 (s, 1 H).

(Cyanomethoxymethyl)triphenylphosphonium bromide was prepared from 2-bromo-2-methoxyacetonitrile in benzene solution by the method of Isler et al.:[44] yield 94%; mp 84–86 °C; ^{1}H NMR (acetone-d_6) δ 3.9 (s, 3 H), 7.7–8.3 (m, 15 H), 9.6 (d, J = 13 Hz, 1 H).

(Cyanomethoxymethyl)triphenylphosphorane. To 10 g (24 mmol) of the above phosphonium bromide in absolute benzene solution was added 2.5 g (24 mmol) of triethylamine dropwise at 25 °C under nitrogen atmosphere and with vigorous stirring. After stirring for 2 h, the white precipitate was filtered off, the solvent evaporated, and the brown residue recrystallized from benzene to afford 7.1 g (88.7%) of the phosphorane: mp 154 °C; ^{1}H NMR (acetone-d_6) δ 3.4 (s, 3 H), 7.4–7.9 (m, 15 H); IR (KBr) 1435 (m), 1180 (s, br), 1115 (s, br), 750 (s), 720 (vs), 695 (vs), 535 (vs, br) cm^{-1}.

Chloroacetaldehyde was prepared in 37% yield by chlorination of ethylenecarbonate,[45] bp 84–87 °C (lit.[45] bp 84–86 °C).

***cis*- and *trans*-4-Chloro-2-methoxycrotononitrile (12a, 12b).** According to the procedure of House et al.[46] 100 g (0.30 mol) of (cyanomethoxymethylene)triphenylphosphorane was reacted with 23.3 g (0.30 mol) chloroacetaldehyde in methylene chloride. The crude product was bulb-to-bulb distilled (100 °C/0.2 mbar) to give 20.0 g (51.3%) of a mixture containing 22% **12a** and 78% **12b**: IR (film) 2230, 2210 (w), 1635 (vs), 1450 (s), 1335 (s), 1270 (s), 1235 (vs), 835 (s), 750 (m), and 685 (s) cm^{-1}. Separation of the cis/trans isomers was achieved by preparative GC on a 3-m aluminum column packed with 5% DEGS on Chromosorb G. Isomeric purity of **12a** and **12b** was 97.9% and 97.3%, respectively (by GC).

12a: ^{1}H NMR (benzene-d_6) δ 3.02 (s, 3 H), 3.53 (d, J = 8 Hz, 2 H), 4.93 (t, J = 8 Hz, 1 H); ^{13}C NMR (benzene-d_6) δ 35.4 (t), 58.3 (q), 112.4 (d), 118.5 (s), 132,3 (s); mass spectrum M$^+$, m/e (relative intensity) 133/131 (2.6/6.8), 118/116 (0.3/1.6, M$^+$ − CH_3), 96 (100, M$^+$ − Cl), 66 (43), 55 (56).

12b: ^{1}H NMR (benzene-d_6) δ 2.70 (s, 3 H), 3.70 (d, J = 8 Hz, 2 H), 4.74 (t, J = 8 Hz, 1 H); ^{13}C NMR (benzene-d_6) δ 39.3 (t), 56.1 (q), 112.6 (d), 119.4 (s), 135.1 (s); mass spectrum identical with that of **12a**.

4-Bromo-2-methoxy-*cis*-crotononitrile (10). **12a** (1.85 g, 6.5 mmol) in 50 mL of absolute benzene solution was stirred for 48 h at 5 °C with 6 g of dry, pulverized NaBr and 0.1 g of dicyclohexyl-18-crown-6. After filtration and evaporation of the solvent the residue was distilled at 40 °C and 0.05 mbar on a Kugelrohr apparatus, giving 1.2 g (69%) of **10**. According to the ^{1}H NMR spectrum (benzene-d_6) the product consists of 93% **10** and 7%. **11**: ^{1}H NMR (benzene-d_6) δ 3.19 (d, J = 1 Hz, 3 H), 3.53 (d, J = 9 Hz, 2 H), 5.17 (t, J = 9 Hz, q, J = 1 Hz, 1 H); ^{13}C NMR (benzene-d_6) δ 22.2 (t), 58.5 (q), 113.1 (d), 119.8 (s), 132.2 (s); mass spectrum M$^+$, m/e (relative intensity) 177 /175 (0.5/0.5), 96 (100, M$^+$ − Br), 66 (40), 55 (61); IR (film) 2230 (w), 1640 (s), 1260 (s), 1210 (s) cm^{-1}.

4-Bromo-2-methoxy-*trans*-crotononitrile (11) was synthesized from 2.5 g of **12b** in the same manner as was **10**: yield 2.2 g (66%). Isomeric purity was approximately 92% (by ^{1}H NMR): ^{1}H NMR (benzene-d_6) δ 2.90 (s, 3 H), 3.71 (d, J = 9 Hz, 2 H), 5.05 (t, J = 9 Hz, 1 H); ^{13}C NMR (benzene-d_6) δ 26.8 (t), 56.6 (q), 112.5 (2), 113.3 (d), 135.0 (s); IR (film) 2250 (w), 1640 (s), 1260 (s), and 1210 (s) cm^{-1}; mass spectrum identical with that of **10**.

***cis*- and *trans*-Propenyl Methyl Ether** were prepared according to Damico[47] by isomerization of allyl methyl ether in 50% yield, bp 45 °C. Separation of the stereoisomers was achieved by preparative GC at 23 °C on a 2-m glass column (15% Squalan on Chromosorb G). Isomers **8** and **9** were pure by 99.2% and 98.3%, respectively.

8: ^{1}H NMR (CCl_4) δ 5.75 (d, J = 6 Hz, 1 H), 4.15 (d, J = 6 Hz, q, J = 6 Hz, 1 H), 3.55 (s, 3 H), 1.6 (t, J = 1 Hz, 3 H).

9: ^{1}H NMR (CCl_4) δ 6.2 (d, J = 12 Hz, q, J = 1.5 Hz, 1 H), 4.5 (d, J = 13 Hz, q, J = 7 Hz, 1 H), 3.45 (s, 3 H), 1.5 (t, J = 1 Hz, 3 H).

2-Vinyl-1,3-dioxolane was prepared from acroleine by standard procedures:[48] bp 62–66 °C (150 mbar) (lit.[49] 115–116 °C); ^{1}H NMR ($CDCl_3$) δ 3.9 (m, 4 H), 5.1–6.2 (m, 4 H).

3,3-Dimethoxypropene (acrolein dimethyl acetal) was synthesized from acrolein and methanol[48] in 43% yield: bp 88–89 °C; ^{1}H NMR (CCl_4) δ 3.2 (s, 6 H), 4.7 (d, 1 H), 5.0–5.8 (m, 3 H).

2-Methoxycrotononitrile was prepared from (cyanomethoxymethyl)triphenylphosphonate and acetaldehyde in 43% yield as described above. Separation of cis/trans isomers was achieved by distillation on a 1-m spinning-band column.

2-Methoxy-*cis*-crotononitrile: bp 37–39 °C (25 mbar); ^{1}H NMR (CCl_4) δ 1.85 (d, J = 8 Hz, 3 H), 3.65 (s, 3 H), 5.5 (q, J = 8 Hz, 1 H).

2-Methoxy-*trans*-crotononitrile: bp 46–47 °C (22 mbar); ^{1}H NMR (CCl_4) δ 1.65 (d, J = 8 Hz, 3 H), 3.7 (s, 3 H), 5.45 (q, J = 8 Hz, 1 H).

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft. Stimulating discussions with Professor Viehe and his group are gratefully acknowledged.

Registry No. 1, 88057-21-0; **6**, 53547-98-1; **7**, 88057-22-1; **8**, 62393-42-4; **10**, 88057-27-6; **11**, 88057-28-7; **12a**, 88057-25-4; **12b**, 88057-26-5; 2-bromo-2-methoxyacetonitrile, 59463-57-9; (cyanomethoxymethyl)triphenylphosphonium bromide, 88057-23-2; (cyanomethoxymethyl)triphenylphosphorane, 88057-24-3; 3,3-dimethoxypropene, 6044-68-4; 2-methoxy-*cis*-crotononitrile, 88083-25-4; 2-methoxy-*trans*-crotononitrile, 88057-29-8; chloroacetaldehyde, 107-20-0; *cis*-propenyl methyl ether, 4188-68-5; *trans*-propenyl methyl ether, 4188-69-6; 2-vinyl-1,3-dioxolane, 3984-22-3; tributylstannyl radical, 20763-88-6.

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