J. Am. Chem. Soc. 1981, 103, 4483–4489

be explained by assuming an encounter complex is involved in the quenching act. The micelle's environment is very polar and results in a decrease in the equilibrium constant for formation of this complex.

**Acknowledgment.** This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation and the National Science Foundation (No. ISP-8011453).

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# [1-$^2$H]Allyl Radical: Barrier to Rotation and Allyl Delocalization Energy

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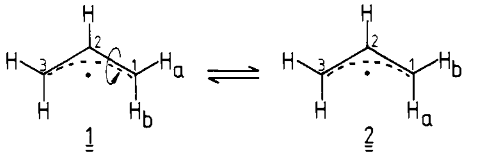
**Abstract:** Syn and anti [1-$^2$H]allyl radicals are generated from deuterated allyl phosphites by attack of *tert*-butoxy radicals, and their interconversion is studied in the temperature range of 50–110 °C. Steady-state kinetic analysis together with time-resolved measurements of the diffusion-controlled recombination kinetics yield an allyl rotational barrier of 15.7 ± 1.0 kcal/mol (log $A$ = 13.5 ± 0.5). From this a value of 14.0–14.5 kcal/mol is deduced for the allyl delocalization energy.

The stereomutation (**1** ⇌ **2**) of allyl radicals, observed for the first time by Walling and Thaler[1] and later detected several times,[2–6] is of importance with respect to synthetic work involving allyl radicals and it is also connected to the problem of allyl delocalization energy.

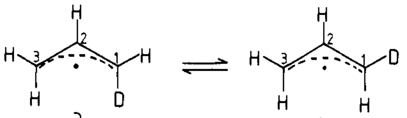


**1** **2**

The qualitative observations provoked quantitative studies[7–12] to determine rotational barriers in these radicals. Table I records values which have been reported so far. Besides the first entry for 1-methylallyl radical, the values were obtained by electron spin resonance (ESR) methods, and in most cases $E_a$ has been evaluated.

Attempts to determine the rotational barrier for the unsubstituted allyl radical by line-shape analysis of its ESR spectrum have failed so far. In experiments, the temperature region where line-shape effects might occur could not be reached.[13] From these studies a lower limit of 17 kcal/mol for the rotational barrier was deduced (for a discussion of this value, see below).

We now report an investigation for an "almost" unperturbed allyl radical that uses a kinetic procedure developed by Hamilton and Fischer for the neophyl rearrangement.[14] The method, also applied to the isomerization of *syn*-1-*tert*-butylallyl radical and the *syn-anti*-1-cyanoallyl radicals (Table I), requires the distinction of syn and anti 1-substituted allyl radicals. This was achieved by incorporating deuterium stereospecifically in the 1 position. Isomerization of **3** and **4** as a function of temperature enables the determination of the energy barrier. The close connection of this value with allyl delocalization energy will be discussed.

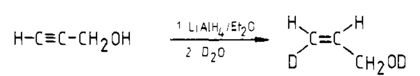


**3** **4**

## Radical Generation

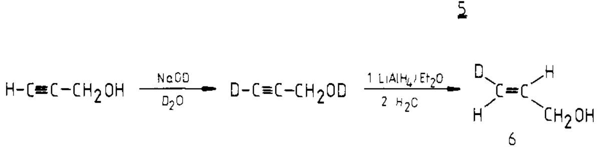
Even though the allyl radical is stabilized, it belongs to the class of transient radicals. An ESR spectroscopic study, therefore, has to be carried out under conditions of continuous radical generation. Triallyl phosphite as radical precursor proved to be most suited for our analysis. Photolysis of di-*tert*-butyl peroxide in the presence of triallyl phosphite has been shown to yield **1** selectively in high concentration at temperatures >−90 °C.[15,16]

Selectively deuterated triallyl phosphites were obtained in 48–67% yield by the reaction of deuterated allyl alcohols with phosphorus trichloride.[17] Cis and trans deuterated allyl alcohols were prepared according to eq 1 and 2. Contrary to reports in



$$\mathrm{H{-}C{\equiv}C{-}CH_2OH} \xrightarrow[2\ \mathrm{D_2O}]{1\ \mathrm{LiAlH_4/Et_2O}} \mathrm{(H)(D)C{=}C(H)(CH_2OD)} \quad (1)$$

**5**



$$\mathrm{H{-}C{\equiv}C{-}CH_2OH} \xrightarrow[\mathrm{D_2O}]{\mathrm{NaOD}} \mathrm{D{-}C{\equiv}C{-}CH_2OD} \xrightarrow[2\ \mathrm{H_2O}]{1\ \mathrm{LiAlH_4/Et_2O}} \mathrm{(D)(H)C{=}C(H)(CH_2OH)} \quad (2)$$

**6**

literature,[18,19] the reduction of sterically nonhindered propargylic alcohols does not proceed stereospecifically. $^1$H NMR, $^{13}$C NMR, IR, and high-resolution mass spectrometry indicated for **5** and **6** the presence of allyl alcohols which were deuterated in different positions. The isomer distribution, however, could not be determined accurately by these techniques. The ESR spectra of the

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[1] C. Walling and W. A. Thaler, *J. Am. Chem. Soc.* **83**, 3877 (1961).

[2] W. A. Thaler, A. A. Oswald, and B. E. Hudson, *J. Am. Chem. Soc.* **87**, 3877 (1961).

[3] W. P. Neumann, H.-J. Albert, and W. Kaiser, *Tetrahedron Lett.*, 2041 (1967); W. P. Neumann and R. Sommer, *Liebigs Ann. Chem.* **701**, 28 (1967); H.-J. Albert, W. P. Neumann, W. Kaiser, and H.-P. Ritter, *Chem. Ber.* **103**, 1372 (1970).

[4] D. B. Denney, R. M. Hoyte, and P. T. McGregor, *J. Chem. Soc., Chem. Commun.*, 2041 (1967).

[5] R. M. Hoyte and D. B. Denney, *J. Org. Chem.*, **39**, 2607 (1974).

[6] I. B. Afanas'ev, I. V. Mamontova, I. M. Filipova, and G. I. Samokhvalov, *Zh. Org. Khim.* **7**, 866 (1971).

[7] R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Am. Chem. Soc.*, **93**, 3810 (1971). This value may be in error, due to wall effects in the kinetic measurements (R. J. Crawford, private communication).

[8] P. J. Gorton and R. Walsh, *J. Chem. Soc., Chem. Commun.*, 783 (1972).

[9] R. Sustmann and H. Trill, *J. Am. Chem. Soc.* **96**, 4343 (1974).

[10] R. Sustmann, H. Trill, F. Vahrenholt, and D. Brandes, *Chem. Ber.*, **110**, 255 (1977); the difference to the activation parameters reported in ref 10 stems from the improved determination of the activation energy for recombination.

[11] R. Sustmann and D. Brandes, *Chem. Ber.* **109**, 354 (1976).

[12] B. E. Smart, P. J. Krusic, P. Meakin, and R. C. Bingham, *J. Am. Chem. Soc.* **96**, 7382 (1974).

[13] P. J. Krusic, P. Meakin, and B. E. Smart, *J. Am. Chem. Soc.* **96**, 6211 (1974).

[14] E. J. Hamilton Jr. and H. Fischer, *Helv. Chim. Acta* **76**, 795 (1973).

[15] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.* **91**, 3944 (1969).

[16] A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1066, (1976).

[17] K. Sasse, *Methoden Org. Chem.* (Houben-Weyl) **12**(2), 55 (1973).

[18] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[19] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis", Butterworth, London, 1955, p 29.

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Table I. Activation Parameters for Isomerization of Substituted Allyl Radicals (kcal mol$^{-1}$)

| | log *A* | $E_a$ | $\Delta G^{\ddagger}$ | method | ref |
|---|---|---|---|---|---|
| *syn*-$CH_2=CH-\dot{C}HCH_3$ | | | 21 | *a* | 7 |
| | | | 14.3 | *b* | 8 |
| $CH_2=C(C(CH_3)_3)-\dot{C}(CN)_2$ | 13.18 ± 0.23 | 9.6 ± 0.3 | 9.0 ± 0.1 | *c* | 9 |
| *syn*-$CH_2=CH-\dot{C}HCN$ | | 10.6 ± 1.3 | | *d* | 10 |
| *anti*-$CH_2=CH-\dot{C}HCN$ | | 9.8 ± 1.1 | | *d* | 10 |
| *syn*-$CH_2=CH-\dot{C}HC(CH_3)_3$ | | 10.3 ± 0.9 | | *d* | 11 |
| $CF_2=CH-\dot{C}F_2$ | | 7.2 | | *c* | 12 |
| $CF_2=CF-\dot{C}F_2$ | | 6.1 | | *c* | 12 |
| $CF_2=CCl-\dot{C}F_2$ | | 4.5 | | *c* | 12 |

[a] Thermolysis of azo compounds. [b] Reaction of HI with butadiene. [c] Dynamic ESR spectroscopy. [d] Steady-state ESR analysis.

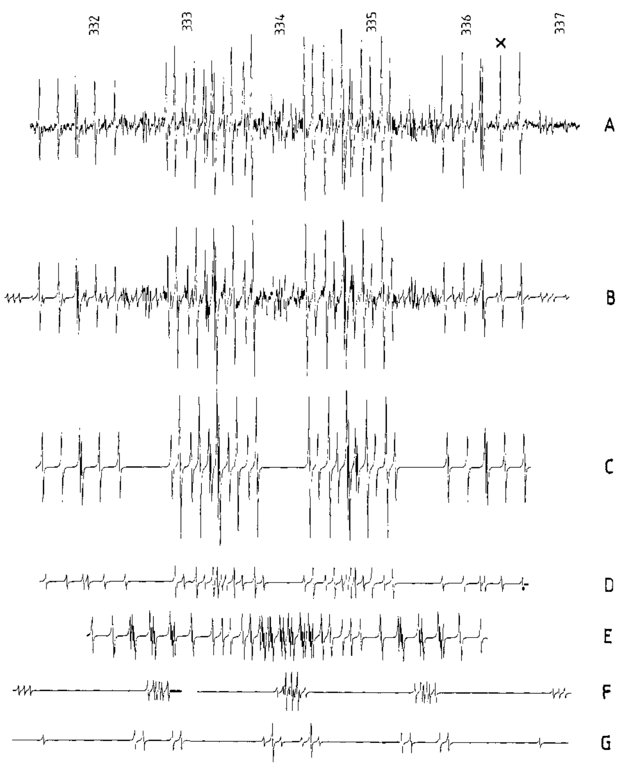


**Figure 1.** ESR spectrum of *syn*-[1-$^2$H]allyl radical **3** at -60 °C: (A) experimental spectrum (field markers in mT), (B) simulated spectrum as superposition of C, D, E, F, and G in the given relative weight, (C) *syn*-[1-$^2$H]allyl radical (58%), (D) *anti*-[1-$^2$H]allyl radical (9%), (E) [1,1-$^2H_2$]allyl radical (22.5%), [2-$^2$H]allyl radical (8%), (G) allyl radical (2.5%).

allyl radicals, however, allowed a quantitative analysis of the isomer composition. An explanation for the formation of cis, trans, and 2-deuterated allyl alcohols during the reduction of undeuterated propargylic alcohol can be provided.[20]

Figures 1 and 2 show the ESR spectra that were obtained at -60 °C. Table II lists the coupling parameters and *g* values. As indicated in the figures, the experimental spectra were properly simulated by superimposing the spectra of different deuterated allyl radicals and the undeuterated allyl radical in the given relative weight.

## Barrier to Isomerization of 3 and 4

Equations 3-7 (Scheme I) give an account of the relevant reactions if the phosphite with a *cis*-[3-$^2$H]allyl group as the major component is used as starting material for the deuterated allyl radical.

Reactions 3-7 occur under steady-state conditions, i.e., the average concentration of individual radicals remains constant ($dc/dt = 0$). For the sake of simplicity, in the derivation of the kinetic equations radicals c, d, and e are treated as one common allyl radical c. This is justified as their recombination rate should be independent of the presence of deuterium.

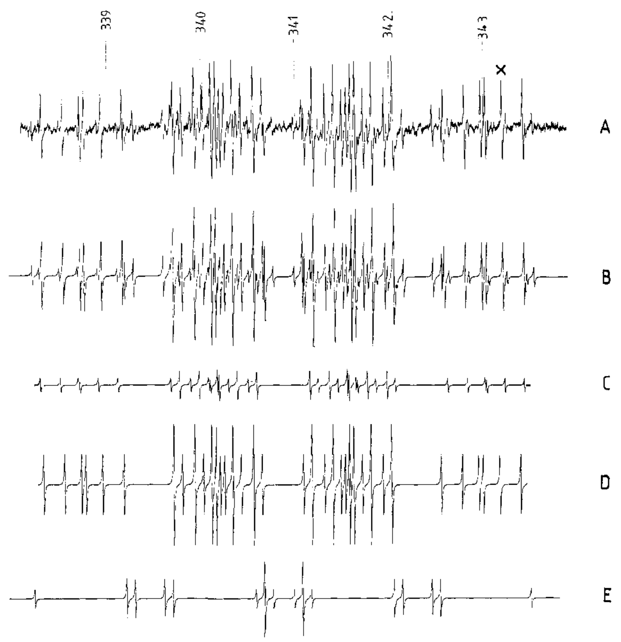
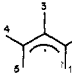
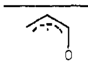
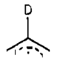
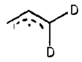


**Figure 2.** ESR spectrum of *anti*-[1-$^2$H]allyl radical **4** at -60 °C: (A) experimental spectrum (field markers in mT), (B) simulated spectrum as superposition of C, D, and E in the given relative weight, (C) *syn*-[1-$^2$H]allyl radical (14%), (D) *anti*-[1-$^2$H]allyl radical (68%), (E) allyl radical (18%).

Table II. ESR Data for Allyl Radicals at -60 °C

|  | *g* factor (±0.00003) | $a_1$[b] | $a_2$ | $a_3$ | $a_4$ | $a_5$ |
|---|---|---|---|---|---|---|
|  | 2.00257 | 0.212 | 1.484 | 0.405 | 1.484 | 1.392 |
|  | 2.00257 | 1.391 | 0.225 | 0.404 | 1.483 | 1.391 |
|  | 2.00256 | 1.392 | 1.482 | 0.063 | 1.482 | 1.392 |
|  | 2.00258 | 0.215 | 0.228 | 0.407 | 1.485 | 1.397 |
|  | 2.00255 | 1.392 | 1.481 | 0.406 | 1.481 | 1.392 |
|  | 2.00254 | 1.390 | 1.481 | 0.406 | 1.481 | 1.390[a] |

[a] Lit. 21, 130 °C. [b] All values are given in mT (±0.002 mT).

The addition of *tert*-butoxy radicals to trialkyl phosphites has been studied kinetically.[22] The rate constants $k_2$ and $k_3$ for addition and cleavage of the phosphoranyl radical are known for R = methyl, ethyl, isopropyl, and *tert*-butyl. In these cases, the addition step is fast and irreversible, while the cleavage is slow. If R = allyl, or benzyl, the rates of the two steps are reversed.

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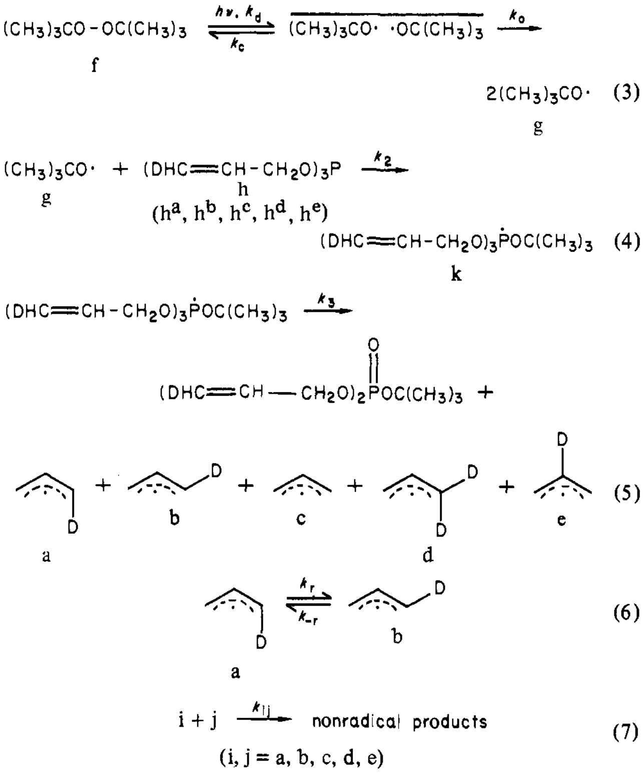
(20) B. Grant and C. Djerassi, *J. Org. Chem.*, **39**, 968 (1974).

(21) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **90**, 7157 (1968).

(22) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

Scheme I



Above −90 °C no phosphoranyl radical can be observed, i.e., β-elimination takes place very rapidly.[15,23] The overall rates of reactions 4 and 5, therefore, will be governed solely by the rate of addition of *tert*-butoxy radical to phosphite.

Product analyses indicate that no products of combination of *tert*-butoxy radicals with other radicals are formed. Cross-termination reactions with *tert*-butoxy radicals, therefore, can be neglected. Furthermore, no evidence for fragmentation of *tert*-butoxy radicals in methyl radical and acetone could be detected. In the kinetic formalism also, no account has to be made for combination reactions with the intermediate phosphoranyl radical as its concentration remains too low even for detection by ESR spectroscopy.

Therefore, only radicals a, b, c, and g are left in the kinetic scheme. For the system tri-*cis*-[3-²H]allyl phosphite/*syn*-[1-²H]allyl radical, one obtains the following steady-state equations where we introduced $k_r = k_{-r}$, i.e., deuterium substitution does not affect the barrier. $I = k_2[g][h^a]$ stands for the rate of formation of allyl radicals.

$$d[a]/dt = I - (2k_{aa})^{1/2}[a]\{(2k_{aa})^{1/2}[a] + (2k_{bb})^{1/2}[b] + (2k_{cc})^{1/2}[c]\} - k_r([a] - [b]) = 0 \quad (8)$$

For *anti*-[1-²H]allyl radical, one obtains

$$d[b]/dt = k_r([a] - [b]) - (2k_{bb})^{1/2}[b][...] = 0 \quad (9)$$

where we used the abbreviation

$$[...] = (2k_{aa})^{1/2}[a] + (2k_{bb})^{1/2}[b] + (2k_{cc})^{1/2}[c] \quad (10)$$

The reactions of allyl radical c, where c is used as the sum of c, d, and e, are given by

$$d[c]/dt = L - (2k_{cc})^{1/2}[c][...] = 0 \quad (11)$$

where $L = k_2[g][h^c]$ (rate of formation of allyl radical c). The brackets symbolize eq 10. *tert*-Butoxy radical obeys

$$d[g]/dt = 2K - I - L = 0 \quad (12)$$

where $K = -d[f]/dt$ represents the rate of the photolytic formation of *tert*-butoxy radical.

Transformation of these equations with respect to the ratio [a]/[b] and inserting $k_r = A_r \exp(-E_a/RT)$ leads, after rearrangement and taking the logarithm, to eq 13 as the final equation.

$$\log [([a]/[b] - 1)/(2K2k_{bb})^{1/2}] = -\log A_r + E_a/2.3RT \quad (13)$$

$E_a$ can now be determined from the ratio [a]/[b] or [b]/[a] as a function of temperature and from a consideration of the temperture dependence of the other quantities in eq 13. The importance of the term $2K$ will be discussed in more detail. Using eq 12, we obtain

$$2K = k_2[g][h^a] + k_2[g][h^c] \quad (14)$$

The rate constant $k_2$ for the addition of *tert*-butoxy radical to triallyl phosphite has not been measured. A good approximation is $k_2' = 6.7 \times 10^9 \exp(-2240/RT)$ M$^{-1}$ s$^{-1}$, where $k_2'$ represents the rate constant for addition of *tert*-butoxy radical to triethyl phosphite.[22] The concentration [h] under our experimental conditions was 25% by volume or approximately 1 M. According to the ESR analysis (see above), this corresponds to 58% tri-*cis*[3-²H]allyl phosphite ([h$^a$]), to 9% tri-*trans*-[3-²H]allyl phosphite ([h$^b$]) and to 31% for the sum of the other triallyl phosphites ([h$^c$]). The total steady-state concentration of the allyl radicals was 1.2–1.0 × 10$^{-6}$ M. This has to be apportioned to the different allyl radicals a, b, and c, depending on their contribution to the mixture. The steady-state concentration of g can be determined to [g] = 6–2 × 10$^{-11}$ M[24] in the temperature range of 50–110 °C. With these quantities we evaluated $2K$ for each temperature where [a]/[b] or [b]/[a] was measured. The denominator of eq 13, furthermore, includes $2k_{bb}$, the rate constant for dimerization of *anti*-[1-²H]allyl radical. Neglecting any isotope effect, we obtained by time-resolved ESR experiments the relation $2k_{bb} = (5.95 \pm 0.27) \times 10^{11} \exp[(-2860 \pm 200)/RT]$ M$^{-1}$ s$^{-1}$. Equation 13 can be simplified to eq 15 when the Arrhenius equation is introduced for $2k_{bb}$.

$$\log\{([a]/[b] - 1)/[(2K)^{1/2}]\} = (E_a - E_{bb}/2)/2.3RT - \log A_r - \tfrac{1}{2} \log A_{bb} \quad (15)$$

The isomerization a ⇌ b (**3** ⇌ **4**) was followed by ESR spectroscopy in the temperature range of 50–108 °C, where either **3** or **4** were the initial main radical. The intensity ratio of the two radicals was obtained from the pair of lines marked by a cross in Figures 1 and 2 because no other lines interfere in this region. The line separation is 0.025 mT. The ratio of the line intensities was determined by comparison of the measured lines with computer-simulated line pairs of given ratios. These values do not yet correspond to the true ratio which follows from isomerization. Both radicals contain a fraction of the other isomer because of the preparation procedure of the deuterated allyl alcohol. At −75 °C, where no isomerization is detectable, the ratio of **3** to **4** with "tri-*cis*-[1-²H]allyl phosphite" as substrate is 7.6 ± 0.3; with the other substrate, the ratio **4**:**3** is 7.7 ± 0.2. These values allowed the calculation of the true intensity ratios due to isomerization. Least-squares analysis yields an activation energy for isomerization of $E_a$ = 15.7 ± 0.4 kcal/mol and a log $A_r$ of 13.5 ± 0.5. The log $A_r$ value falls in the range for unimolecular isomerizations with negligible entropy contribution and conforms with log $A_r$ for the isomerization of 1,1-dicyano-2-*tert*-butylallyl radical (see Table I). Figure 3 displays the experimental points and the calculated regression line.

## Time-Resolved Measurements and Product Analysis

For the application of eq 15, a value of $E_{bb}$, the activation energy of combination of allyl radicals under our experimental conditions, is needed. Other studies either in the gas phase[25] or in liquids of low viscosities[26,27] had shown that allyl radicals terminate by combination to 1,5-hexadiene. Dimerization outweighs by far any

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(23) W. G. Bentrude in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, p 623.

(24) Evaluation is based on the fact that all *tert*-butoxy radicals are converted to allyl radicals as shown by product analysis, using $[t\text{-BuO}\cdot] = 2k_{bb}[\text{allyl}]^2/k_2[\text{triallyl phosphite}]$, which follows from combination of eq 4 and 7.

(25) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).

(26) R. Klein and R. D. Kelley, *J. Phys. Chem.*, **79**, 1780 (1975).

(27) D. L. Baulch, P. K. Chown, and D. C. Montague, *Int. J. Chem. Kinet.*, **11**, 1055 (1979).

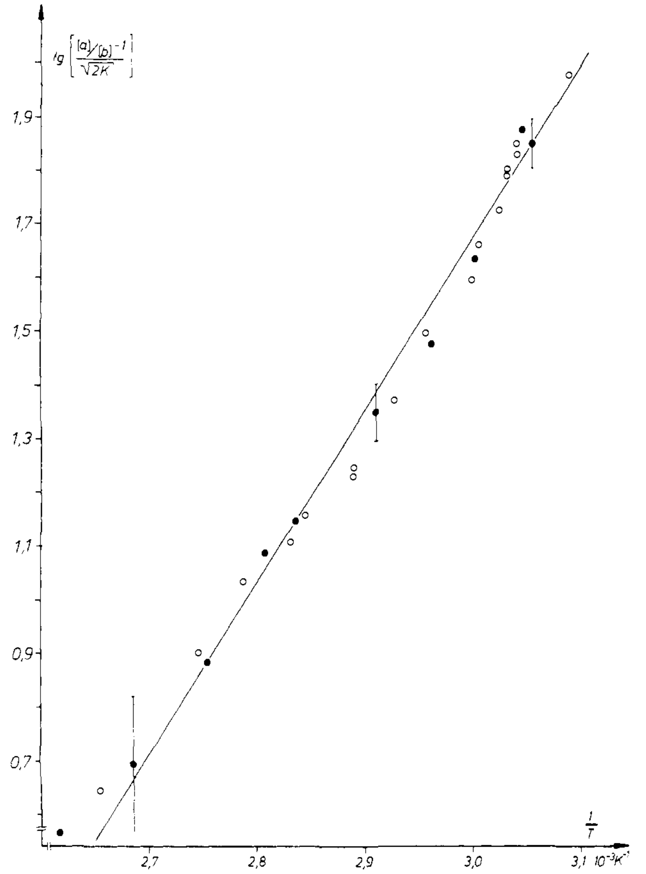

**Figure 3.** Isomerization **3** ⇌ **4** as f($T$): (○) isomerization **3** → **4**, (●) isomerization **4** → **3**.

other termination reaction. Hefter et al.[28] also had investigated the kinetics of combination in solvents of low viscosity by time-resolved measurements. In liquid propene the activation energy for dimerization is 1.2 kcal/mol. Rate constants of $10^9$–$10^{10}$ $M^{-1}$ $s^{-1}$ support a diffusion-controlled reaction.

For the measurement of the self-termination and for the product analysis, the allyl radical was generated by photolyzing a mixture (percent volume) of 40% undeuterated triallyl phosphite, 30% di-*tert*-butyl peroxide, and 30% chlorobenzene. During the measurement, the solution was pumped (0.2 mL/min) through a flat quartz cell (optical path length, 0.7 mm). Time-resolved measurements were carried out as described in the Experimental Section. The decay curves were analyzed on the basis of a bimolecular self-termination of the allyl radical. Rate constants at different temperatures are collected in Table III. The graphical representation of log ($2k_t$) vs. $1/T$ to obtain the activation energy for recombination (Figure 4) does not give a straight line. The curvature in the region of 30–60 °C can be approximated by a superposition of two straight lines as is indicated in the figure. This behavior can be explained if an additional termination reaction comes into play above 30 °C. Other explanations like experimental errors or a temperature dependence of the $A$ factor were excluded.

In order to estimate the extent of this side reaction, we carried out careful product analyses. Equal amounts of an oxygen-free mixture (percent volume) of 40% triallyl phosphite, 30% di-*tert*-butyl peroxide, and 30% dichlorobenzene were photolyzed for 10 min under conditions of the ESR experiments at different temperatures. The VPC analysis is given in Figure 5. The main results of this analysis are: (a) no products of thermal decomposition of *tert*-butoxy radicals are obtained, (b) no products (>0.2%) were found which are the result of combination of allyl radical with other low-molecular-weight radicals, (c) there is no indication for the formation of disproportionation or H-abstraction products of the allyl radical, (d) the formation of 1,5-hexadiene parallels the consumption of di-*tert*-butyl peroxide (DTBP), (e) the amount of diallyl *tert*-butyl phosphate (DATBPO) is smaller (10–20%) than is calculated from the consumption of DTBP and from the formation of 1,5-hexadiene, (f) the percentage of triallyl phosphite decreases with increasing temperature much faster than would be anticipated either from the formation of DATBPO and 1,5-hexadiene or from the decrease in DTBP, and (g) the relative amount of chlorobenzene in the photolyzed solution becomes greater with increasing temperature.

Table III. Second-Order Rate Constants $2k_t$ for the Self-Termination of Allyl Radicals

| temp, °C | $2k_t$,[a] ($10^9$ $M^{-1}$ $s^{-1}$) | SD[b] | $r^2$[c] |
|---|---|---|---|
| −38.1 | 0.43 | 0.01 | 0.995 |
| −37.2 | 0.42 | 0.01 | 0.997 |
| −18.7 | 0.64 | 0.01 | 0.997 |
| 2.4 | 0.96 | 0.03 | 0.998 |
| 22.6 | 1.43 | 0.04 | 0.997 |
| 41.8 | 2.15 | 0.09 | 0.991 |
| 62.6 | 3.51 | 0.01 | 0.990 |
| 79.7 | 4.76 | 0.19 | 0.986 |
| 99.8 | 6.70 | 0.13 | 0.977 |
| 117.9 | 9.25 | 0.22 | 0.984 |

[a] Mean value from four decay curves. [b] Standard deviation. [c] Measure of determination.

As no further low-molecular-weight products are identifiable above 40 °C, there remains as only explanation for the additional termination reaction a process by which allyl radicals react with triallyl phosphite under formation of polymeric material. This is supported by the increase in triallyl phosphite consumption at elevated temperatures which is not paralleled by a corresponding increase in low-molecular-weight products. The side reaction was tentatively considered in the kinetic scheme for isomerization of [1-$^2$H]allyl radicals. As its influence turned out to be negligible, it was left out in the final analysis.

Time-resolved measurements together with product analysis lead to a value of 2.76 ± 0.06 kcal/mol (log $A$ = 11.18 ± 0.02) for the activation energy of combination of two allyl radicals (40% triallyl phosphite, 30% DTBP, 30% chlorobenzene, by volume). This is based on an analysis of the kinetic measurements between −38.1 and 22.6 °C. If one carries out this evaluation for a solution of the same composition as that for the determination of the isomerization barrier (25% triallyl phosphite, 30% DTBP, 45% chlorobenzene, by volume), $E_a$ amounts to 2.86 ± 0.20 kcal/mol (log $A$ = 11.77 ± 0.05). For both solutions, the dynamic viscosities were measured. The viscosity–temperature relations obey the law of Andrade with $E_\eta$ = 2.45 ± 0.02 kcal/mol and $E_\eta$ = 2.58 ± 0.10 kcal/mol, respectively. The agreement with the values from time-resolved measurements supports the diffusion-controlled combination of allyl radicals in these solutions.

## Discussion

A critical assessment of the barrier to rotation requires a thorough discussion of possible errors. The standard deviation represents the errors due to uncertainties in the ratio [a]/[b] and in the variation of the actual probe temperature. These have been taken into account in the evaluation of the regression line of Figure 3.

Hamilton and Fischer[14] in their treatment of the neophyl rearrangement neglected the term $2K$ (eq 14) and estimated under their assumptions and approximations a total error for the activation energy (10.3 kcal/mol) of ±2 kcal/mol. If in our evaluation the term $2K$ is omitted, the barrier to rotation is reduced by 0.9 kcal/mol. As the consideration of $2K$ should not increase the error but rather should diminish an error, we can presume that our standard deviation of ±0.4 kcal/mol takes care of this error source. Cage recombination[29] of *tert*-butoxy radicals as a source of error

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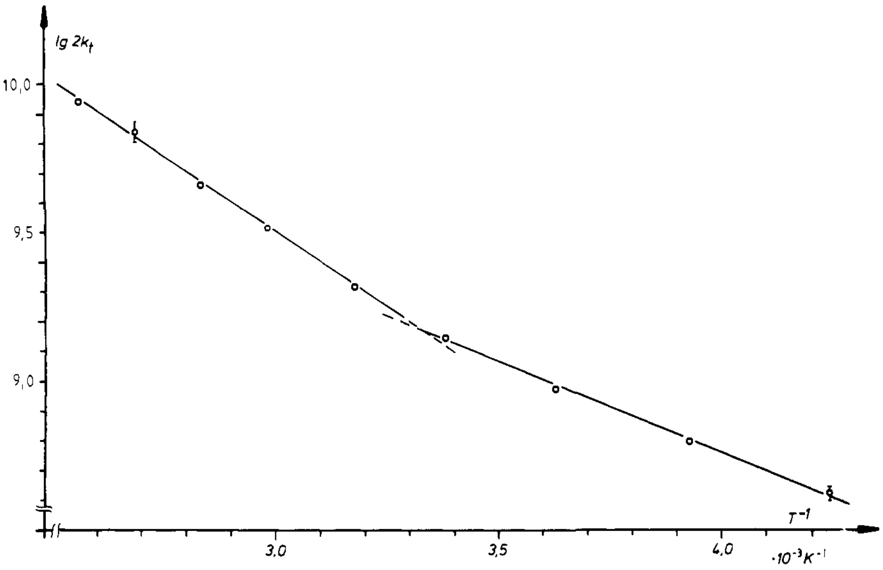

Figure 4. $1/T$ vs. log $(2k_t)$ diagram for the termination of allyl radicals in 40% triallyl phosphite solution.

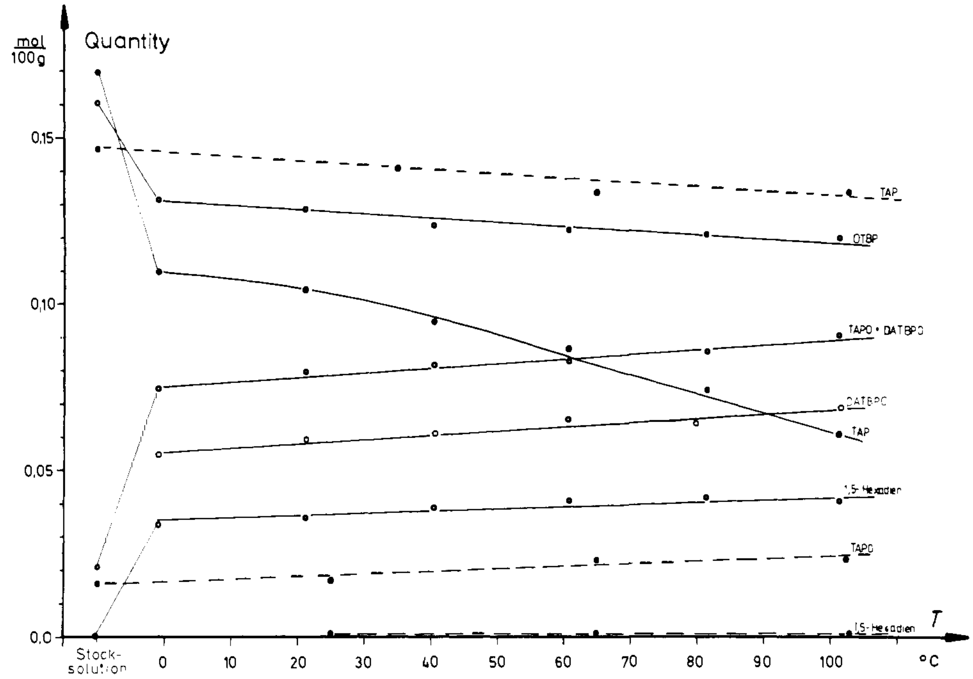

Figure 5. Product analysis of photolyses of triallyl phosphite as f($T$). (–) Photolysis in the presence of DTBP; (---) photolysis in the absence of DTBP. TAP = triallyl phosphite, TAPO = triallyl phosphate, DATBPO = diallyl *tert*-butyl phosphate, DTBP = di-*tert*-butyl peroxide.

can be neglected. The rate of formation of the *tert*-butoxy radicals in our temperature range proves to be constant.[30,31] A systematic error in the determination of the syn/anti ratio of the radicals by different saturation behavior and a CIDEP effect also was excluded.

Taking into consideration these points, one arrives at the conclusion that the error limit might be higher than the standard deviation but it should not exceed ±1 kcal/mol. The barrier to rotation therefore is *15.7 ± 1.0 kcal/mol.*

From attempts to determine the rotational barrier by dynamic ESR spectroscopy, a lower limit of 17 kcal/mol had been estimated.[13] This estimation was based on experiments for which, supposedly, the spectrum of the allyl radical had been recorded, not disturbed by line shape effects, at 280 °C. Careful reexamination, using the same substrates and solvents, showed that it is impossible to reach 280 °C *inside* the probe and to record a spectrum at the same time. We failed to surpass 200–210 °C because bubbling due to rapid decomposition of DTBP prevented any recording even of single lines.

**Allyl Rotational Barrier and Allyl Delocalization Energy.** The interaction of a double bond with an adjacent center bearing an electron in a p orbital has fascinated chemists over many years. For recognition of the relationship between allyl rotational barrier and allyl delocalization energy, the different notions have to be precisely stated.

The desired quantity can be recognized in Figure 6. The energy content of the delocalized structure relative to the noninteracting localized forms is lowered by $\Delta E$ = ADE (allyl delocalization energy). As experimental measures, two quantities were used initially:[32] allyl resonance energy[33] (ARE) and allyl stabilization energy (ASE).[34]

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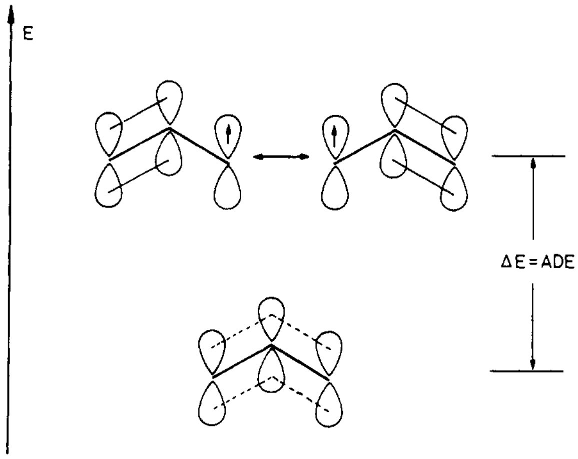
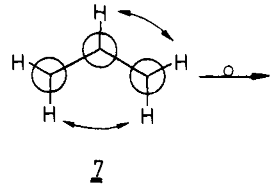


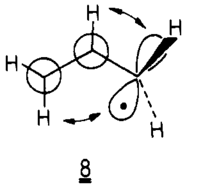
**Figure 6.** Definition of allyl delocalization energy (ADE).

ARE is defined as the difference in bond dissociation energy (BDE) of a primary C–H bond in propene and methane, whereas ASE uses propane as the reference system. The formation of the radicals by hydrogen abstraction from precursors is accompanied by changes in bond strengths of the $\sigma$ skeleton which are not directly affected. They only can be evaluated approximately[35] as they are not accessible experimentally. Besides some mass spectrometric determinations[36] of ARE and ASE, most values derive from applications of thermochemical kinetics.[37] Reported values range from 9 to 25 kcal/mol.[33,34,36,38]

In order to arrive at an unambiguous and experimentally easily verifiable definition, the allyl rotational barrier (ARB) was suggested as a measure for ADE.[35,39] In the transition state for rotation, the vinyl group and the p orbital carrying the unpaired electron are orthogonal to each other. The barrier is determined by two processes: the loss in delocalization energy, which should provide the main contribution, and the barrier to rotation about a CC-$\sigma$ bond.



**7**



**8**

A further differentiation may be useful. We will call the rotational barrier in a symmetrical allyl radical ARB, whereas the barrier to isomerization in an unsymmetrically substituted allyl radical will be termed allyl isomerization barrier (AIB). The latter distinction is made because in these cases the barrier syn/anti may not be identical with that of the interconversion anti/syn (see for example 1-*tert*-butylallyl radical[11]).

Which relationship does exist between our measured barrier (AIB) in [1-$^2$H]allyl radicals and the quantities ARB, ADE, ARE, and ASE? In the absence of significant isotope effects, AIB should be equal to ARB. The Arrhenius activation energy $E_a$ is a macroscopic quantity, whereas ADE is defined microscopically. The macroscopic value $E_a$ has as its counterpart in the microscopic area the threshold energy $E_0$.[40] This does not need to be identical with $E_a$. Considering an ARB of 15.7 ± 1.0 kcal/mol and a temperature range of 50–100 °C, one can estimate[40] that $E_a/E_0$ corresponds to about 1.03, i.e., the thereshold energy $E_0$ is lower than $E_a$ by 0.4–0.5 kcal/mol.

The connection between threshold energy and ADE is established when a correction for the barrier to rotation about an allylic sp$^2$–sp$^2$ single bond without $\pi$ interaction is made. Because no experimental verification of this quantity is possible, we only can make reasonable assumptions. **7** and **8** display two relevant conformations of the allyl radical. As far as H–H interactions are concerned, **8** rather than **7** should be a minimum in the potential energy curve. If we include the half-filled p orbital, then **8** should be destabilized because two hydrogen atoms are eclipsed with the p orbital. As one knows from the minimum conformation of the propyl radical,[41] a radical prefers eclipsing of hydrogen atoms or of hydrogen and a methyl group instead of a conformation where H atom and p orbital are eclipsed (hyperconjugative effect). This indicated that **8** might possess a higher energy content than **7**. From the fact that the barrier in alkyl radicals is low, one may conclude that H–H interactions and hyperconjugative destabilization are similar. Therefore a $C_{sp^2}$–$C_{sp^2}$ barrier to rotation also should be low. An indication of this may be seen in the low barrier to rotation in the central bond in biphenyl (<1 kcal/mol).[42] This admittedly crude discussion leads to a value for ADE which is about 1 kcal/mol below the threshold energy, i.e., ADE according to our analysis should be 14.0–14.5 kcal/mol.

A value of 14.0–14.5 kcal/mol for ADE is at the upper limit of more recent determinations by other methods. Most often values are given which derive from differences in activation parameters and provide a measure for differences in ground-state energies. A very careful analysis of cis/trans isomerization of hexatrienes gives ADE as 12.2 or 13.1 ± 2 kcal/mol depending on the reference system (ethene or *trans*-2-butene).[35] A similar thermochemical cycle on the basis of allene isomerizations yielded 14.0 ± 2 kcal/mol.[43] In both investigations ADE is determined as the difference of activation parameters. Benson and Golden and collaborators who determined values for ASE from differences in bond dissociation energies[34,38c,e,f,k,p] arrive at the conclusion that ASE cannot exceed drastically 12 kcal/mol.[38p] In several publications, Trenwith reports values for ASE close to 12.6 kcal/mol.[38q,s,w]

## Experimental Section

**ESR Measurements.** X-band spectrometers Varian E-3 and Bruker ER-420 were used. Radicals were generated by UV photolysis of di-*tert*-butyl peroxide (DTBP) in the cavity of the spectrometer in the presence of substrates. UV-light sources were a 1-kW mercury high-pressure lamp, Philips SP-1000, and a 1-kW Hg/Xe high-pressure lamp (Hanovia 977B-1). The light beam was focused by means of a Suprasil–quartz lens system. Visible and infrared components were eliminated

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through a water-cooled uranium glass filter (UG-5, Schott & Gen.) or by means of a cooled filter solution (1.14 M of $NiSO_4$ + 0.21 M of $CoSO_4$ in $H_2O$, 3-cm path length).

Highest purity commercially available solvents were employed. DTBP was filtered over neutral $Al_2O_3$ (Woelm) by using a 2 × 10 cm packed column. Halogen-containing solvents were purified by chromatography on basic aluminum oxide.

All measurements were carried out in a flow system where a motor driven syringe (50-mL volume) pumps the solution with constant flow (0.03–1 mL/min) through the cell in the cavity. The Suprasil-made cells are either flat cells (8 × 30 mm parallel plates; optical pathlength, 0.4, 0.7, or 1.0 mm) or circular tubes, closed at one side, where a capillary connected to the syringe is used to introduce the solution. The latter arrangement was used to determine the ratio of **3** and **4** as f($T$) because higher signal intensities could be achieved. Temperature measurements were made by a thermoelement (Chromel/Alumel, 0.25 mm $\phi$) which was inside the cell and which could be moved to the actual place of radical detection in the cavity. Temperature regulation occurred by means of standard equipment (Varian or Bruker) ($T$ variations, ±1 °C). During the steady-state kinetic measurement the light was filtered by the above-mentioned filter solution and a UG-5 filter. This reduced the temperature increase during illumination to 3 °C at the most.

The actual solutions were composed of 25 vol % tri-*trans*, *cis*-[3-$^2$H]allyl phosphite (98% by GC), 30 vol % DTBP (>99% by GC), and 30 vol % chlorobenzene (>99.9% by GC). The solutions were made oxygen free by purging them for 60 min with nitrogen. Kinetic measurements were made with a flow of 0.2 mL/min.

The ratio **3**/**4** was evaluated on the basis of two hyperfine lines separated by 0.025 mT (indicated by crosses in Figures 1 and 2), which are not disturbed by lines of other radicals present. These lines were recorded 5–9 times (0.1 mT/40 cm chart paper) at a given temperature. The latter was determined inside the illuminated area of the cell before and after each recording. The temperature variation never exceeded ±1 °C.

The determination of the ratio **3**/**4** was carried out by computer simulation. From the experimental spectra, the height of the lines, the line width, and the line separation was extracted. Using these parameters, we calculated line pairs (Lorentzian line shape) which corresponded most closely to the experimental conditions. After correction for 100% pure isomer composition, the regression line of Figure 3 was evaluated with the programm ACTPAR.[44]

**Time-Resolved ESR Experiments.** The optical system is based on the equipment for the experiments with steady irradiation. A quartz lens system focuses the light beam in the plane of a rotating sector and then parallels it before it is focused again on the cavity of the spectrometer. The rotating sector consists of an aluminum disk ($\phi$ 200 mm, 3 mm thick) with a 90° sector for illumination. The frequency of rotation (170–200 Hz, ±1 Hz) is monitored by a photodiode and a frequency counter. The signal is accumulated in a CAT (Varian C-1024) which is triggered by the rotating sector. The measurements are made in a dual cavity. After 100-kHz phase-sensitive detection, the signal is given directly to the CAT from where it is finally displayed on a XY recorder.

Measurements were carried out under conditions of slow flow (0.2 mL/min). The signal and the base line were accumulated for equal periods of time, and the temperature was measured inside the cell with a 0.25-mm thermoelement which could be moved to the center of the cell inside the cavity.

Absolute radical concentrations were determined for each temperature by recording part of the spectrum under continuous irradiation and by comparing it with a signal of a calibrated standard (Varian strong pitch) after numerical integration of the best-fitted simulated spectrum.

**Viscosity Measurements.** Dynamic viscosities of the solutions for the kinetic experiments were determined with a kugelfall viscosimeter. The temperature dependence of $\eta$ is given by (a) 40% triallyl phosphite/30% DTBP/30% chlorobenzene: $\log(\eta/cp) = -(1.831 \pm 0.014) + (2450 \pm 2)/2.3RT$ ($r^2 = 0.999$) and (b) 25% triallyl phosphite/30% DTBP/45% chlorobenzene: $\log(\eta/cp) = -(2.018 \pm 0.004) + (2580 \pm 10)/2.3RT$ ($r^2 = 0.999$).

**Product Analysis.** Samples (0.5 mL) of an oxygen-free solution of 40% (vol) triallyl phosphite, 30% (vol) di-*tert*-butyl peroxide, and 30% (vol) chlorobenzene in sealed quartz tubes ($\phi$ 5 mm) were irradiated under the conditions of the ESR experiment for 10 min at different temperatures (UV source, Hanovia 977B-1 with UG-5 filter). The sample tubes rotated at 100 cycles/min. GC analysis was done on a SE-30 (10%) column on chromosorb WHP 80/100 mesh (injector temperature, 150 °C; detector temperature, 180 °C; oven temperature, 5 min at 40 °C; temperature increase, 30 °C/min, 17 min at 180 °C). Identification of products occurred by comparison with authentic samples. Quantitative determinations were based on measured area factors. By comparison with authentic samples it was shown that no allyl alcohol, acetone, and allyl *tert*-butyl ether were present. Compounds with retention times greater than that of triallyl phosphate could not be detected even at 240 °C.

Under the same conditions a product analysis of a sample, irradiated in absence of DTBP [40% triallyl phosphite, 60% chlorobenzene (v/v)] was performed.

**Preparation of Deuterated Allyl Phosphites. *cis*-[3-$^2$H]Allyl Alcohol.** To a suspension of 30 g (0.84 mol) of $LiAl\mathbf{H}_4$ in 1500 mL of absolute ether, 47.2 g (0.84 mol) of propargylic alcohol was added slowly under vigorous stirring ($N_2$ atmosphere). The temperature was kept at −15−−5 °C. The suspension was stirred for 4 h at 0 °C and for 15 h at room temperature. After the suspension was cooled to −10 °C, 67 g (3.4 mol) of $D_2O$ was added slowly. After 4 h, the precipitate was filtered and washed several times with absolute ether. The combined solutions were dried over $MgSO_4$, and ether was distilled off over a 1-m column; yield, 47.6 g (94%). According to GC, the product contained 3.9% propargylic alcohol and 2.1% *n*-propanol. Distillation on a spinning band column yielded a product of 99% purity 32.5 g (63.7%): bp 98 °C (97 °C, undeuterated[45]); IR (NaCl) 3060 (m, $\nu_{=C-H}$), 3010 (m, $\nu_{=C-H}$), 2490 (vs, b, $\nu_{O-D}$), 2260 (w, $\nu_{=C-D}$), 1625 (w, $\nu_{C=C}$) cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ 3.95 (d, $J$ = 5.5 Hz, 2 H, $=CCH_2O$), 4.98 (d, $J$ = 10.4 Hz, t, $J$ = 1 Hz, 0.77 H, $=C\mathit{H}D$), 5.1–5.3 (m, 0.16 H, undeuterated and/or trans deuterated compound; $^{13}$C NMR ($C_6D_6$) $\delta$ 63.1 ($=C\mathit{C}H_2O$), 113.2, 114.4, 115.4 (t, $J$ = 23.5 Hz, $=CHD$); 114.5 (s, $=CH_2$); 114.6, 115.1 ($=CD_2$); 137.8 (s, $=\mathit{C}H(CH_2)$; 136.8 ($=\mathit{C}D(CH_2)$. Mass spectrum (70 eV), *m*/*e* (rel intensity) 61 (7), 60 ($M^+$, 32), 59 (90), 58 (95), 57 (100), 56 (27), 55 (32), 54 (15), 44 (21), 43 (81), 42 (27), 41 (59), 40 (38), 39 (40), 38 (10), 37 (7), 31 (53), 30 (45), 29 (71), 27 (33).

**Tri-*cis*-[3-$^2$H]allyl Phosphite.** *cis*-[3-$^2$H]Allyl alcohol (46.9 g, 0.78 mol) was reacted with 35.7 g (0.26 mol) of $PCl_3$ and 86 g (0.86 mol) of triethylamine in 300 mL of absolute benzene, according to literature.[17] Yield after distillation on a 10-cm Vigreux column was 29.8 g (55.8%, lit.[17] 67%); bp 36–38 °C (0.1 mm) [lit. mp 58–60 °C (0.8 mm)]; $^1$H NMR ($CCl_4$) $\delta$ 4.25 (d, d, d, $J$ = 8.7, 5.5, 1 Hz, 2 H, $=CCH_2OP$), 5.05 (d, t, $J$ = 10.0, 1.0 Hz, 1 H, $=C\mathit{H}D$), 5.7–6.1 (m, 1 H, $=C\mathit{H}(CH_2)$); $^{13}$C NMR ($C_6D_6$) $\delta$ 62.8, 63.3 ($J$ = 10.3 Hz, $O\mathit{C}H_2CH=$), 114.6, 115.7 ($J$ = 23.5 Hz, $-C=\mathit{C}HD$), 135.1, 135.3, 135.4 ($J$ = 2.9 Hz, $-CH_2C\mathit{H}=CHD$); additional peaks from tri-*cis*-[3-$^2$H]allyl phosphate: $\delta$ 68.0, 67.6 (d, $J$ = 5.7 Hz, $P-O-\mathit{C}H_2-CH=$), 117.3, 117.5, 118.4 (t, $J$ = 23.5 Hz, $=CHD$), 133.0, 133.1, 133.4 (t, $J$ = 2.9 Hz, $CH_2-\mathit{C}H=CHD$); GC–MS, (rel intensity) 163 (5.3), 147 (4.7), 123 (10), 122 (7.1), 107 (8.8), 106 (11.2), 85 (5.9), 84 (21.1), 83 (37.6), 82 (29.4), 81 (32.9), 80 (18.8), 70 (5.9), 69 (12.9), 68 (9.4), 59 (12.9), 58 (30.6), 57 (12.4), 56 (15.9), 55 (11.2), 47 (8.2), 44 (11.2), 43 (100), 42 (98.9), 41 (25.9), 40 (39.5), 38 (17.6), 31 (21.2).

**[1,3-$^2$H$_2$]Prop-2-en-1-ol.** Propargic alcohol (60 g, 1.1 mol) was reacted 5 times with 100 mL of freshly prepared 1 N $NaOD/D_2O$ solution. The deuterated product was isolated through addition of dry NaCl; yield, 46 g (77%); degree of deuteration according to $^1$H NMR, >98%.

***trans*-[3-$^2$H]Allyl Alcohol.** [3-$^2$H]Propargylic alcohol (46 g, 0.79 mol) in 250 mL of absolute ether was reacted with 20 g (0.53 mol) of $LiAlH_4$ in 2 L of absolute ether and 25 mL of $D_2O$, according to the procedure for the preparation of *cis*-[3-$^2$H]allyl alcohol: yield, 25.1 g (53.4%); bp 97–98 °C (lit.[45] bp 97 °C, undeuterated); IR (NaCl) 2290 (w, $\nu_{=CD}$) cm$^{-1}$; $^1$H NMR ($C_6D_6$) $\delta$ 4.05 (s, br, 2 H, $=C-CH_2-$), 4.65 (s, 1 H, OH), 5.20 (d, t, $J$ = 18 Hz, 1 H, $=C\mathit{H}D$), 5.90 (m, d, $J$ = 18 Hz, 1 H, $=C\mathit{H}(CH_2)$. From the integration of the signals at 5.20 ppm follows ~20% undeuterated and cis deuterated product.

**Tri-*trans*-[3-$^2$H]allyl Phosphite.** *trans*-[3-$^2$H]Allyl alcohol (11.7 g, 0.2 mol), 8.9 g (0.07 mol) of $PCl_3$, and 22 g (0.22 mol) of triethylamine yielded, according to the above procedure for tri-*cis*-[3-$^2$H]allyl phosphite, 20.4 g (58.4%) of product: bp 42–44 °C (0.2 mm) [lit.[17] bp 58–60 °C (0.8 mm)]: IR (NaCl) 3060, 3040, 3020 (w, $\nu_{=CH}$), 2280 (w, sh, $\nu_{=CD}$), 1625 (m, $\nu_{C=C}$) cm$^{-1}$; $^1$H NMR ($C_6D_6$) $\delta$ 4.25 (m, $J$ = 8.0, 5.0, 1.5 Hz, 2 H, $= CCH_2O$), 5.2 (d, t, $J$ = 17, 1.5 Hz, 1 H, $=C(D)\mathit{H}$), 5.7 (m, d, $J$ = 17, 1.5, 5.0 Hz, 1 H, $=C(\mathit{H})CH_2$).

**Acknowledgment.** This work was supported by the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and by Deutsche Forschungsgemeinschaft.

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