123

PHOTOINDUCED FRAGMENTATION OF β-HYDROXYALKYL-*tert*-BUTYL PEROXIDES: AN ELECTRON SPIN RESONANCE INVESTIGATION

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Summary

UV irradiation of the β-hydroxydialkyl peroxides $(CH_3)_3COOCH_2CH_2OH$ and $(CH_3)_3COOCH_2CHCH_3OH$ is shown to generate the radicals $\cdot CH_2OH$, and $\cdot CH_2OH$ and $CH_3\dot{C}HOH$ respectively. A scheme is proposed comprising photodecomposition and the subsequent fast thermal fragmentation of the primary photoradicals leading to the hydroxyalkyl radicals.

1. Introduction

During some attempts to generate the 2-hydroxyethoxy radical (3) by photodissociation of 2-[(1,1-dimethylethyl)dioxy]ethanol (1) (2-*tert*-butylperoxyethanol) in aprotic solvents we observed electron spin resonance (ESR) spectra which could not be assigned to radical 3 but rather to a fragment of it:

1   2   3
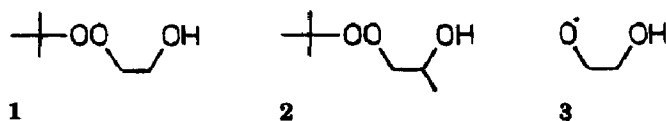
A better insight into this unexpected finding was obtained by performing a similar experiment with 1-[(1,1-dimethylethyl)dioxy]-2-propanol (2) (1-*tert*-butylperoxy-2-propanol) which was found to behave analogously to compound 1.

β-hydroxyalkyl-*tert*-butyl peroxides have been subjected to only a few investigations [1, 2]. In this report we propose a mechanism, which is believed to be general, for their photoinduced fragmentation in aprotic solvents.

2. Experimental details

Compounds 1 and 2 were prepared by the reaction of *tert*-butylhydroperoxide with ethylene oxide and 1,2-propene oxide respectively according to the method of Barusch and Payne [3]. The structure of the peroxide resulting from 1,2-propene oxide was proved to be 2 by ^{13}C nuclear magnetic resonance. The isomer $(CH_3)_3COOCH(CH_3)CH_2OH$ could not be detected. The radicals were generated in a flow system by irradiating a 5×10^{-2} mol dm^{-3} solution of the corresponding peroxide in benzene using an HBO 500 W Osram lamp. A detailed description of the full instrumentation has been given elsewhere [4].

3. Results

Figure 1 shows the ESR spectrum which was obtained by irradiation of a solution of 1 in benzene at room temperature. The pattern can be interpreted in terms of two isotropic coupling constants $a_1 = 0.07$ mT and $a_2 = 1.74$ mT, and the spectrum can clearly be attributed to the hydroxymethyl radical (4) [5] where a_1 is due to the hydroxylic proton and a_2 is due to the α protons:

OH ... H—C·—H ... 4

OH ... H—C·—CH$_3$ ... 5

The ESR spectrum reproduced in Fig. 2 was obtained by photolysis of 2 in benzene at room temperature. The pattern arises from the superposition of
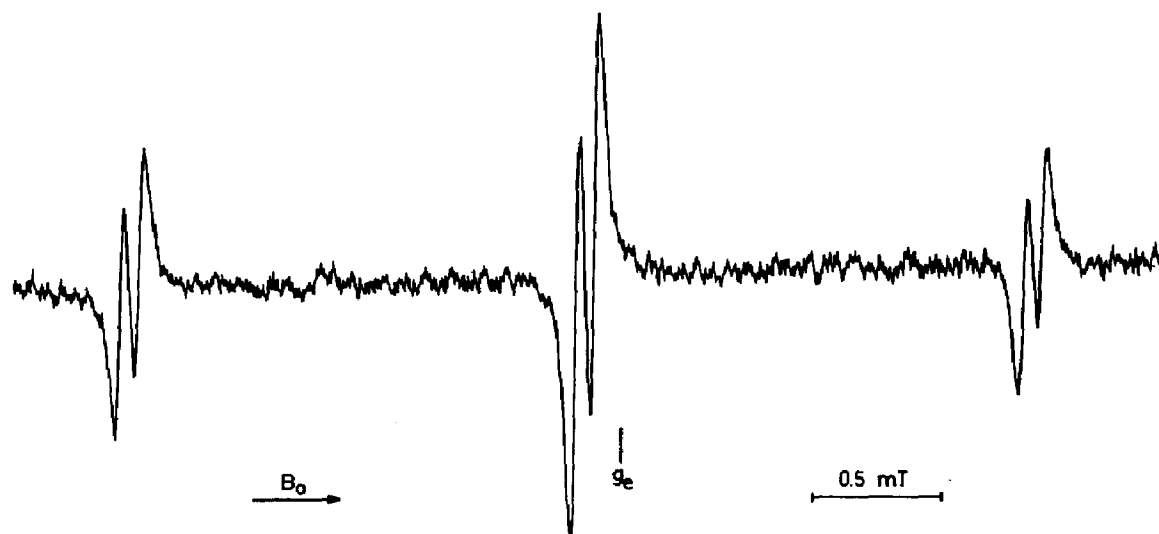

B_0 g_e 0.5 mT

Fig. 1. Photodecomposition of 1: ESR spectrum of the radical 4 obtained by UV irradiation of a 0.05 mol dm^{-3} solution of 1 in benzene at room temperature.
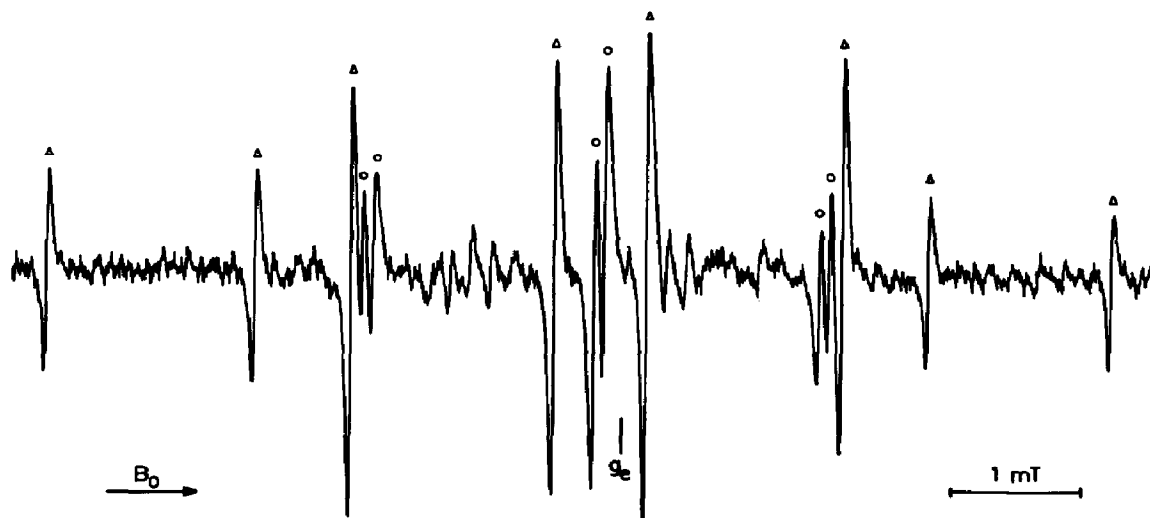
Fig. 2. Photodecomposition of 2: ESR spectrum of a mixture of 4 (○) and 5 (△) obtained by the UV irradiation of a 0.05 mol dm^{-3} solution of 2 in benzene at room temperature.

two distinct ESR spectra. The spectrum composed of the resonance lines marked with open circles is again assigned to 4 while the spectrum labelled with open triangles can undoubtedly be attributed to the 1-hydroxyethyl radical (5) on account of the two isotropic hyperfine coupling constants $a_1 = 1.53$ mT (α proton) and $a_2 = 2.23$ mT (methyl protons). The splitting which originates from the hydroxylic proton is not resolved in this case [4]. The additional lines (unmarked in Fig. 2) could not be assigned.

4. Discussion

The formation of 4 from 1 could be rationalized as follows:

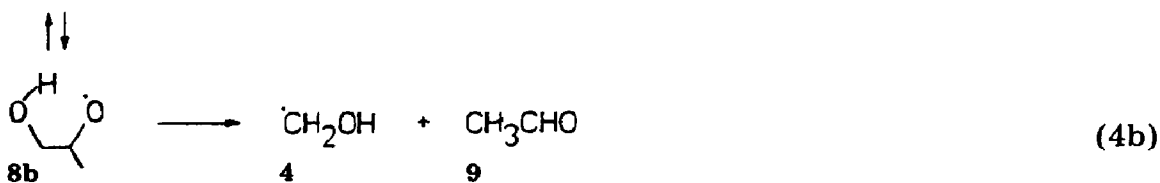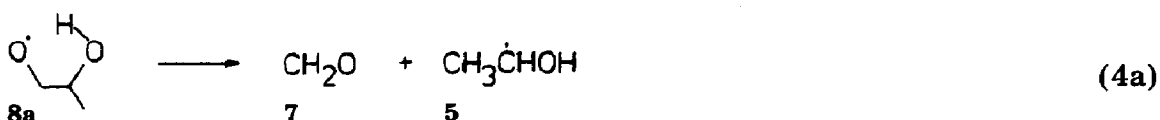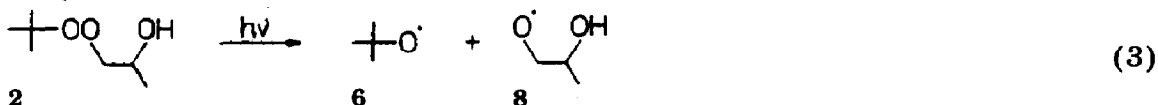$$\text{(1)}$$

$$\text{(2)}$$
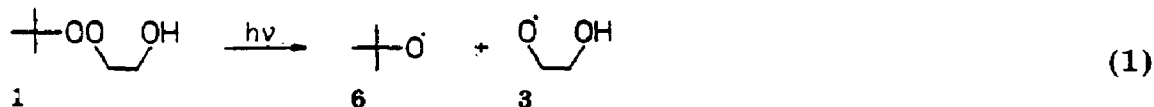
However, a closer inspection raises the question of the structure of the primary radical 3. This radical should exhibit an intramolecular hydrogen bond, so we can ask, on account of the very fast intramolecular hydrogen exchange, whether thermal equilibrium between the fully equivalent structures

3a ⇌ 3b

is established before intermediate 3a decays according to eqn. (2). In practice we cannot distinguish between the fragmentation of 3a and 3b.

This problem can be elucidated on the basis of the photoinduced decay of 2. As stated in Section 3, the photolysis of 2 generates 4 as well as 5. An obvious explanation for this result is given by the mechanism

$$
\underset{\textbf{2}}{+\!OO\diagdown OH} \xrightarrow{h\nu} \underset{\textbf{6}}{+\!O\cdot} + \underset{\textbf{8}}{O\diagdown OH} \tag{3}
$$

$$
\underset{\textbf{8a}}{\overset{H}{O\diagdown O}} \longrightarrow \underset{\textbf{7}}{CH_2O} + \underset{\textbf{5}}{CH_3\dot{C}HOH} \tag{4a}
$$

$$
\updownarrow
$$

$$
\underset{\textbf{8b}}{\overset{H}{O\diagdown O}} \longrightarrow \underset{\textbf{4}}{\dot{C}H_2OH} + \underset{\textbf{9}}{CH_3CHO} \tag{4b}
$$

In this case the inequivalence of the structures of 8a and 8b allows us to postulate an intramolecular hydrogen exchange which is fast enough to compete with the fragmentation reaction (4a). The essential features of the photoinduced decomposition of peroxides 1 and 2 are summarized in the following scheme.

$(R \equiv H, CH_3)$
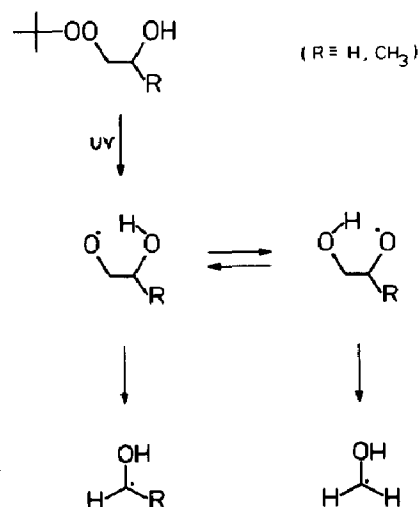
The fact that the primary radicals 3, 6 and 8 have not been observed deserves a brief comment. Radicals with a threefold or higher symmetry axis, *e.g.* radical 6, may have ground states with electronic orbital degeneracy. In this case the interaction of rotational, vibrational and electronic orbital and spin angular momentum leads to complex ESR spectra. In liquid solu-

tion such spectra are not observed owing to large linewidths [6 - 8]. In contrast, the radicals 3 and 8 cannot have electronic orbital degeneracy because of a low symmetry, but still might be undetectable owing to near-orbital degeneracy. Although this argument cannot be discarded, the non-observability of the radicals 3 and 8 is probably due to their very short lifetimes. Little work has been published on radicals of this type, *i.e.* radicals exhibiting intramolecular hydrogen bonds as shown by the structural fragment
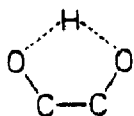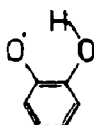

10

Examples of such studies are investigations of the structural and dynamic properties of the intramolecular hydrogen bridges of radicals
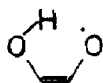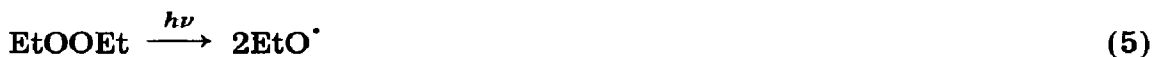

11   **12**

which are obtained by the photoreduction of glyoxal [9] and by hydrogen abstraction from 1,2-dihydroxybenzene [10] respectively. In these radicals some electrons appear to be delocalized, and the corresponding resonance energy may be sufficient to confer on them enough stability to be detected even at room temperature, in contrast with the behaviour of 3 and 8.

To our knowledge there exist no analogous investigations of the dynamic aspects of radicals in which the C—C bond of fragment 10 is saturated. The only report of such radicals is that of Makarov and Ershov [11], who assigned to 3 a poorly resolved ESR spectrum obtained by the γ irradiation of a sample of ethylene glycol and subsequent UV illumination. The existence of 3 has also been postulated by Niki *et al.* [12] for the gas phase oxidation of C_2H_4–NO mixtures initiated by the HO$^\bullet$ radical. According to these workers the decay of radical 3 in the gas phase also follows eqn. (2) but no fast intramolecular hydrogen exchange (see the scheme above) was assumed. Richardson *et al.* [2] have also assumed 2-hydroxyalkoxy radicals to be present in the mechanism of the thermal decomposition of tertiary alkyl peroxides.

To conclude we discuss an alternative mechanism to the above scheme.

When diethyl peroxide is photolysed in carbon tetrachloride, hexane or water the only products obtained are ethyl alcohol and acetaldehyde [13]. These observations can be explained in terms of the following mechanism:
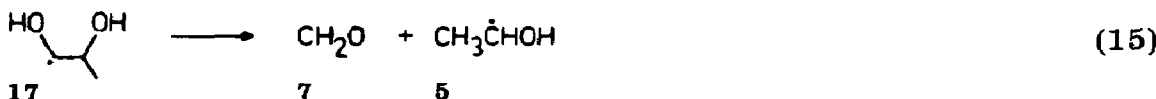
$$\text{EtOOEt} \xrightarrow{h\nu} 2\text{EtO}^\bullet \tag{5}$$

$$\text{EtO}^\bullet + \text{EtOOEt} \longrightarrow \text{EtOH} + \text{EtOO}\overset{\bullet}{\text{C}}\text{HCH}_3 \tag{6}$$

$$EtOO\dot{C}HCH_3 \longrightarrow EtO^{\cdot} + CH_3CHO \tag{7}$$

$$2EtOO\dot{C}HCH_3 \longrightarrow EtOH + 3CH_3CHO \tag{8}$$

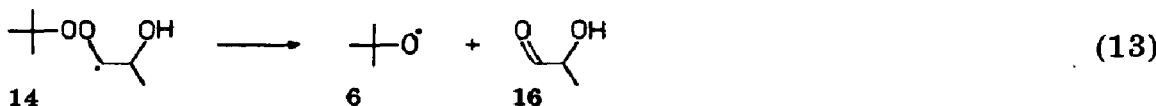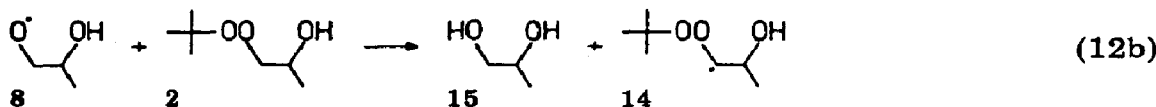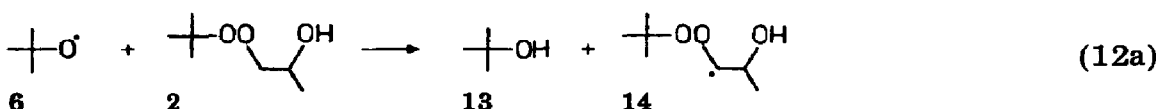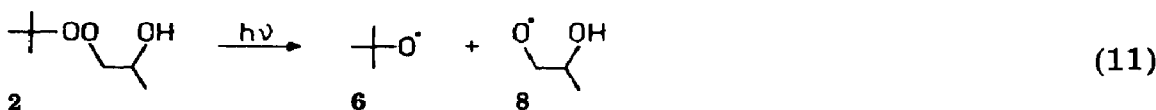$$2EtO^{\cdot} \longrightarrow CH_3CHO + EtOH \tag{9}$$

In view of our discussion, the important feature is the formation of a carbonyl compound, acetaldehyde in this case, which can be further reduced to yield the corresponding hydroxyalkyl radical according to [4]

$$CH_3CHO \xrightarrow[ZH]{h\nu} CH_3\dot{C}HOH \tag{10}$$

where ZH represents a hydrogen donor. By analogy we might therefore explain the formation, for example, of 4 and 5 from peroxide 2 via the following mechanism:

$$\underset{\textbf{2}}{+\!-OO\diagdown OH} \xrightarrow{h\nu} \underset{\textbf{6}}{+\!-O^{\cdot}} + \underset{\textbf{8}}{\dot{O}\diagdown OH} \tag{11}$$

$$\underset{\textbf{6}}{+\!-O^{\cdot}} + \underset{\textbf{2}}{+\!-OO\diagdown OH} \longrightarrow \underset{\textbf{13}}{+\!-OH} + \underset{\textbf{14}}{+\!-OO\diagdown OH} \tag{12a}$$

$$\underset{\textbf{8}}{\dot{O}\diagdown OH} + \underset{\textbf{2}}{+\!-OO\diagdown OH} \longrightarrow \underset{\textbf{15}}{HO\diagdown OH} + \underset{\textbf{14}}{+\!-OO\diagdown OH} \tag{12b}$$

$$\underset{\textbf{14}}{+\!-OO\diagdown OH} \longrightarrow \underset{\textbf{6}}{+\!-O^{\cdot}} + \underset{\textbf{16}}{O\diagdown OH} \tag{13}$$

$$\underset{\textbf{16}}{O\diagdown OH} \xrightarrow[ZH]{h\nu} \underset{\textbf{17}}{HO\diagdown OH} \tag{14}$$

$$\underset{\textbf{17}}{HO\diagdown OH} \longrightarrow \underset{\textbf{7}}{CH_2O} + \underset{\textbf{5}}{CH_3\dot{C}HOH} \tag{15}$$

$$\underset{\textbf{7}}{CH_2O} \xrightarrow[ZH]{h\nu} \underset{\textbf{4}}{\dot{C}H_2OH} \tag{16}$$

Other reactions are also conceivable, but lead essentially to the same conclusions.

The mechanism expressed by eqns. (11) - (16) can be ruled out by the following arguments.

(1) Photoreduction of formaldehyde (see eqn. (16)) in the presence of methylcyclohexane (a good hydrogen donor) was found to yield no detectable concentration of CH_2OH at $-80\,°C$ [4].

(2) For the photolysis of peroxide **1** the above mechanism predicts formation of the glycolaldehyde **18** (see eqn. (13)), which should be photoreduced according to

$$\underset{\textbf{18}}{\overset{O\quad OH}{\diagdown\diagup}}\xrightarrow[ZH]{h\nu}\underset{\textbf{19}}{\overset{HO\quad OH}{\diagdown\diagup}} \tag{17}$$

1,2-dihydroxyethyl (**19**) can indeed be generated by UV irradiation of a sample of ethylene glycol containing 1% H_2O_2, and its ESR spectrum is known [14]. Radical **19** has not been observed in this work. However, the observation of chemically induced dynamic nuclear polarization in the photolysis of glycolaldehyde in aqueous solution by Seifert and Bargon [15] does not lend support to the transient formation of radical **19**. This can be understood if photolysis of aqueous glycolaldehyde involves dissociation of the C—C bond but not photoreduction by hydrogen abstraction. Therefore the radicals observed in this work could in principle be produced by further complex mechanisms involving Norrish type I decomposition.

(3) Measurement of the signal intensity dependence of the two radicals $\dot{C}H_2OH$ (**4**) and $CH_3\dot{C}HOH$ (**5**) on the light intensity clearly shows that formation of both radicals is a one-photon process. This is documented in Fig. 3 in which the peak-to-peak ESR signals of the two radicals **4** and **5** are plotted against the relative radiation power. Figure 3 shows the signal intensity *versus* light intensity curve to be slightly convex, indicating that the fate of the radicals involves second-order termination reactions.

Finally it should be noted that the radicals **4** and **5** are formed from peroxide **2** with approximately the same quantum yields (see Fig. 2). In
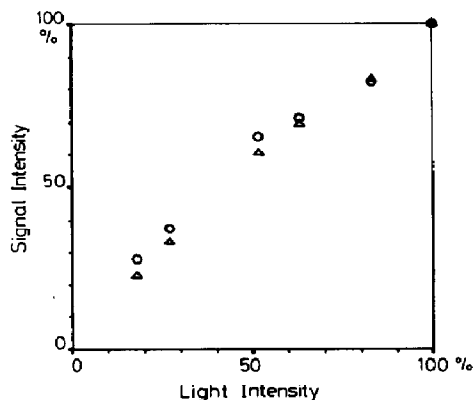

Fig. 3. Dependence of the ESR signal intensity of radicals **4** and **5** on the relative light intensity (room temperature; benzene solution; peroxide concentration, 0.05 mol dm^{-3}): $\bigcirc$, CH_2OH radical; $\triangle$, CH_3CHOH radical.

terms of the first scheme this result suggests that the hydrogen transfer process between 8a and 8b (see eqn. (4)) is much faster than thermal decomposition and that 8a and 8b have almost equal thermodynamic functions.

Acknowledgments

References

1 W. H. Richardson and T. C. Heesen, *J. Org. Chem.*, *37* (1972) 3416.
2 W. H. Richardson, M. B. Yelvington, A. H. Andrist, E. W. Ertley, R. S. Smith and T. D. Johnson, *J. Org. Chem.*, *38* (1973) 4219.
3 M. Barusch and J. Q. Payne, *J. Am. Chem. Soc.*, *75* (1953) 1987.
4 G. Cirelli, T.-K. Ha, R. Meyer and Hs. H. Günthard, *Chem. Phys.*, *72* (1982) 15.
5 J. E. Wertz and J. R. Bolton, *Electron Spin Resonance*, McGraw-Hill, New York, 1972, pp. 53, 59, 205.
6 M. C. R. Symons, *J. Am. Chem. Soc.*, *91* (1969) 5924.
7 J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, *91* (1969) 3940.
8 L. S. Silbert, in D. Swern (ed.), *Organic Peroxides*, Vol. 2, Wiley-Interscience, New York, 1970, p. 725.
9 M. Rudin, K. Loth, F. Graf and Hs. H. Günthard, *Chem. Phys. Lett.*, *46* (1977) 29.
10 K. Loth, F. Graf and Hs. H. Günthard, *Chem. Phys.*, *13* (1976) 95.
11 I. E. Makarov and B. Ershov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, (1970) 485.
12 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *J. Phys. Chem.*, *82* (1969) 135.
13 G. A. Holder, *J. Chem. Soc., Perkin Trans. II*, (1972) 1089.
14 R. Livingston and H. Zeldes, *J. Chem. Phys.*, *44* (1966) 1245.
15 K. G. Seifert and J. Bargon, *Angew. Chem.*, *85* (1973) 768.