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Spin Trapping of Radicals from the Reactions between Donor and Acceptor Olefins. Further Evidence for the Tetramethylene Diradical Intermediate as the Initiator of Spontaneous Copolymerization

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ABSTRACT: EPR spectroscopy and product isolation have been used to investigate the initiation of spontaneous copolymerizations of donor and acceptor monomers. The results establish the presence of tetramethylene diradicals as the only experimentally supported intermediates in the initiation for these spontaneous copolymerizations. No evidence supporting a Mayo cycloaddition mechanism, electron transfer, or charge-transfer complex initiation was found. The reaction of an olefin activated by three electron-accepting groups, such as dimethyl cyanofumarate, methyl 3,3-dicyanoacrylate, or trimethyl ethylenetricarboxylate, with a styrene having unsubstituted ortho positions was used in this study. In the presence of the spin trap 2-methyl-2-nitrosopropane (*t*-BuNO), aminoxyls with characteristic EPR spectra of high intensity were detected. Reaction of 4-methoxystyrene and dimethyl cyanofumarate in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) led to a diamagnetic 1:1:1 adduct, 4-cyano-6-methoxy-3,4-dimethoxycarbonyl-1-piperidinyloxytetrahydronaphthalene, which was subjected to an X-ray crystallographic study. Treatment of the TEMPO adduct with *t*-BuNO in chloroform gave a solution containing TEMPO and the same aminoxyl as that formed from 4-methoxystyrene, dimethyl cyanofumarate, and *t*-BuNO. These aminoxyls were assigned the structure of spin adducts of tetrahydronaphthalen-1-yl radicals, formed by initial trapping of the diradical of the donor and acceptor olefin at the more reactive radical center, followed by cyclization into the aromatic ring. This proposed mechanism provides an alternative to the commonly accepted Mayo initiation mechanism.

Introduction

Although spontaneous homopolymerizations are rare, spontaneous free radical copolymerizations of monomers with different polarities are often encountered. As an example, the spontaneous copolymerization of the electron-rich styrene and electron-poor acrylonitrile has been thoroughly studied.[1,2] Work by Hall and Padias has systematically explored comonomer systems by gradually increasing the donor and the acceptor strength of the donor and acceptor olefin, respectively.[3,4] The observed spontaneous polymerizations varied from spontaneous free radical copolymerizations to ionic homopolymerizations. In this paper, we will focus on the free radical copolymerization systems.

Several suggestions as to the origin of the initiating radicals of the spontaneous polymerizations have been made, ranging from charge-transfer complexes to electron transfer to bond forming initiation involving diradicals[3−6] (Scheme 1). An initiation mechanism for the spontaneous free radical homopolymerization of styrene, originally proposed by Mayo, involves a Diels−Alder cycloadduct as the critical intermediate, followed by H atom transfer to form the initiating radicals, also shown in Scheme 1.[7]

Otsu et al. performed EPR spin trapping experiments to elucidate the mechanism of the spontaneous copolymerizations of vinyl sulfides and electron-poor monomers such as maleic anhydride and acrylonitrile.[8] They postulated preliminary electron transfer from donor to acceptor, followed by proton transfer. The hydro and vinyl radicals were then proposed to initiate the copolymerization. However, these studies were refuted by Mash et al., who investigated the initiation with deuterated vinyl sulfides and showed that trapping of the postulated vinyl radical was untenable.[9]

A similar electron/proton transfer mechanism was held by Otsu to apply to styrene as the donor monomer with three acceptor monomers in the presence of $ZnCl_2$; additionally, a cyclic radical was postulated to originate from a Mayo-type adduct.[10] Eberson and Persson reexamined the reaction of styrene and maleic anhydride in the presence of the spin trap, 2-methyl-2-nitrosopropane (**1**, MNP, *t*-BuNO), in chloroform and observed the buildup of several persistent spin adducts.[11] These were assigned structures in which the growing copolymer had been trapped at radical centers derived from both the styrene and maleic anhydride component. Again, the vinyl radical was excluded as a possible intermediate. Moreover, Eberson and Persson showed from the redox potentials of the reactants that electron transfer was not a feasible mechanism.

Hall and Padias postulated a polar tetramethylene diradical as the true intermediate in such reactions.[3,4] Their studies of the spontaneous alternating copolym-

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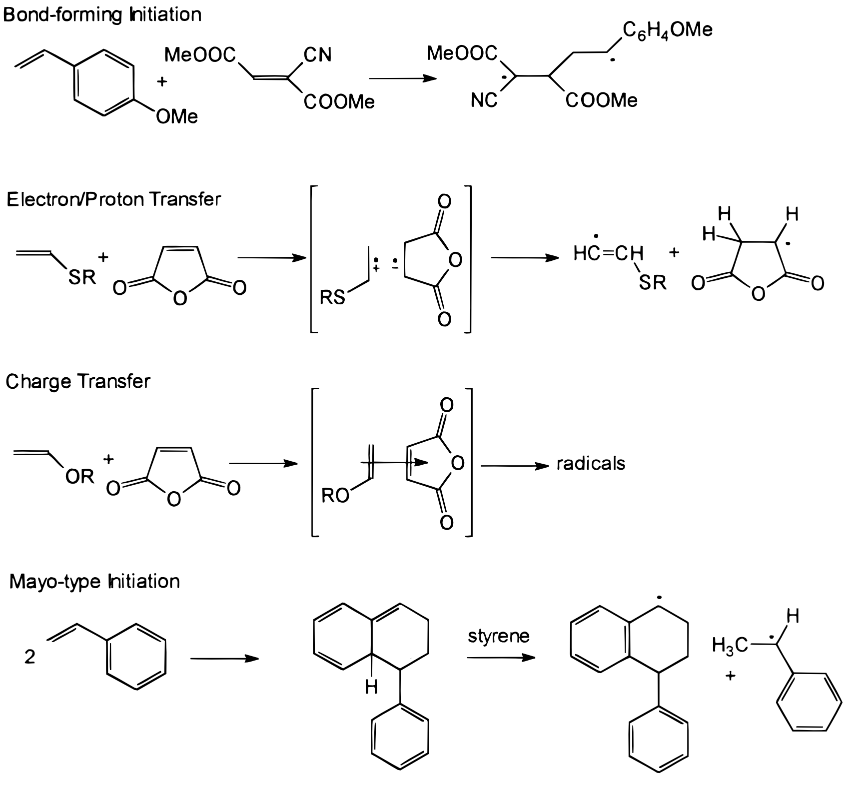
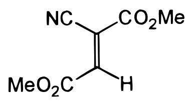
Scheme 1. Postulated Initiation Mechanisms for Spontaneous Free Radical Polymerization in the Literature



erization of 4-methoxystyrene and dimethyl cyanofumarate (**2**) or methyl 3,3-dicyanoacrylate (**3**) strongly supported this postulate.[12] The evidence included both second-order kinetics whose rate constant was not sensitive to solvent polarity and growth of molecular weight with time. In addition it was possible to trap and identify by NMR spectroscopy a stable product (**6**) from **2**, 4-methoxystyrene, and the persistent radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (**7**, TEMPO).[12a] The most likely pathway for formation of **6** involves diradical **4** which is trapped by **7** at the radical center adjacent to the 4-methoxyphenyl group to give radical **5**. Cyclization of **5** followed by oxidation and proton loss to give **6** completes the reaction, as shown in Scheme 2. The tetramethylene diradical intermediate explains the ESR trapping results of Mash et al.,[9] as well as the results of Eberson and Persson,[11] according to these respective authors.

$(CH_3)_3CNO$

1



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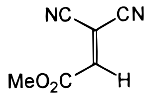
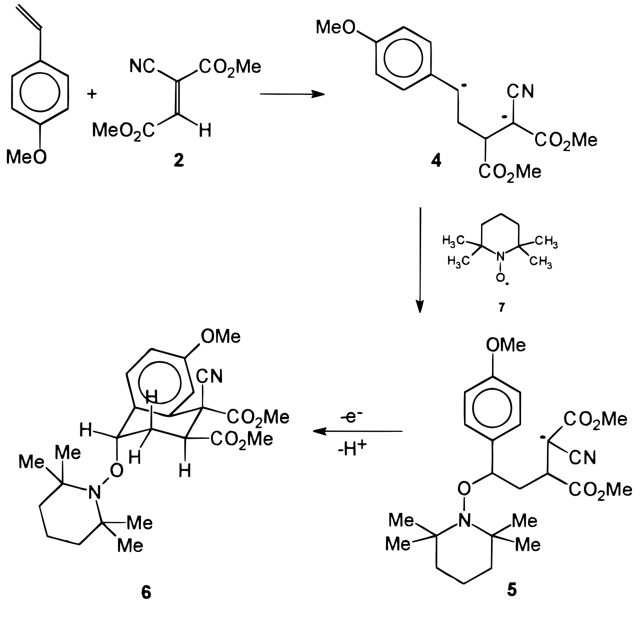


3

To further elucidate the role of the diradical in the initiation of spontaneous copolymerization, trisubstituted acceptor olefins were judged to be best suited. The advantage of using a trisubstituted acceptor olefin lies in the significant stabilization of the radical center substituted with two electron-withdrawing groups, since then the donor olefin-derived radical center will be by far the more reactive one.

In what follows, the reaction between **2**, **3**, or trimethyl ethylenetricarboxylate (**8**) and various styrenes in the presence of **1** is examined by EPR spectroscopy. The results obtained fully corroborate and generalize the tetramethylene diradical hypothesis for such acceptor olefins.

Scheme 2. Proposed Mechanism for the Formation of Adduct 6



Results

X-ray Crystallographic Study of 6. Knowing the correct structure of **6** is crucial for establishing the intermediacy of the diradical. While the NMR spectral characterization of **6** is straightforward,[5a] its structure is complex enough for an X-ray crystallographic determination to be warranted in order to get a definitive proof.

The X-ray crystal structure of **6** was determined at −120 °C (Figure 1). This compound crystallizes in the

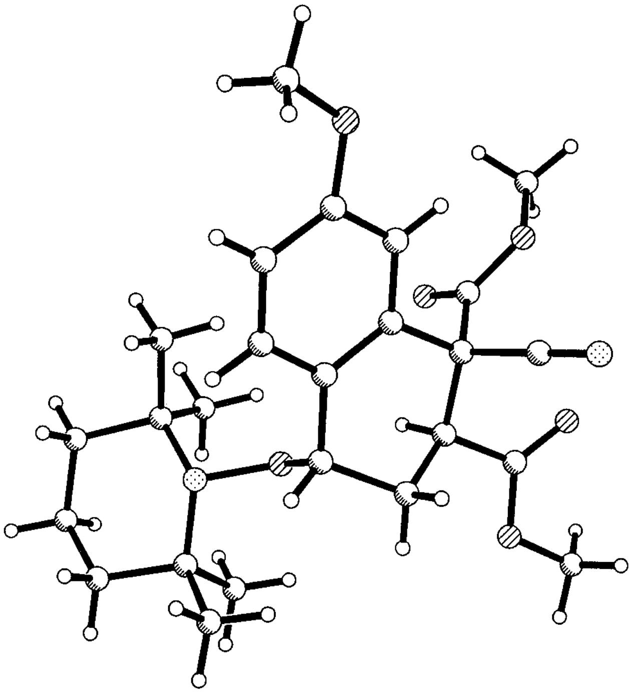


Figure 1. Perspective view of the X-ray crystal structure of **6**.

monoclinic space group $P2_1/c$, with one molecule in the asymmetric unit. The structure is confirmed as that previously proposed,[12a] with the two methoxycarbonyl groups mutually trans and the **7** substituent trans to the nitrile group. Furthermore, in the solid state the molecule exists in a conformation similar to that previously proposed, having the **7** and nitrile groups in axial orientations within the half-chair of the tetralin ring. The plane of the methoxycarbonyl group attached to the quaternary carbon is approximately orthogonal to the tetralin plane, whereas the other methoxycarbonyl group is close to coplanar with the tetralin system. As is usual for **7** substituents, the piperidine ring exists in a chair conformation with the attached oxygen equatorial. All of these conformational effects minimize intramolecular steric interactions. There are no unusually short intermolecular contacts.

Spin Adducts from the Reaction between Substituted Styrenes and 2 or 3. The reaction between **2** (0.26 mol dm^{-3}), 4-methoxystyrene (0.20 mol dm^{-3}), and **1** (0.1 mol dm^{-3}) in $CDCl_3$ directly gave rise to a strong EPR spectrum (Figure 2) which had $a^N = 1.485$, $a^H = 0.212$, $a^{H'} = 0.156$, $a^{H''} = 0.052$ G, and $a^{H'''} = 0.046$ mT. After 20 h, the spectrum was very intense and only the 0.21 mT coupling was distinguishable in each group, presumably due to exchange line broadening. The reaction was also performed with a reactive aromatic compound, 1,3,5-trimethoxybenzene (0.50 mol dm^{-3}) present to possibly trap a radical intermediate in an intermolecular step. The outcome was exactly the same as that in the experiment without 1,3,5-trimethoxybenzene added, and no additional radical spectrum was detected.

Almost identical spectra were obtained from styrene, 4-fluorostyrene, 4-acetoxystyrene, or 3-chlorostyrene in reactions with **1** and **2** (Table 1). With styrene-β,β-d_2, the coupling constants denoted $a^{H'}$ and $a^{H''}$ were the ones replaced by those of deuterium atoms. The spectrum from α-methylstyrene had lost the largest coupling constant a^H, whereas that from trans-β-methylstyrene had lost $a^{H'}$.

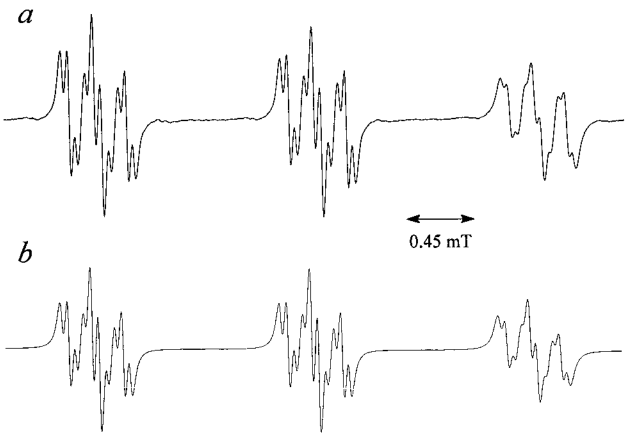
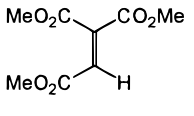


Figure 2. (a) EPR spectrum from a solution of dimethyl cyanofumarate (**2**, 0.26 mol dm^{-3}), 4-methoxystyrene (0.20 mol dm^{-3}), and **1** (0.10 mol dm^{-3}) in (^{2}H)chloroform. (b) Simulation based on the parameters given in the text.

Closely similar spectra were obtained with **3** (Table 1). The EPR spectral parameters were nearly identical, irrespective of the nature of the acceptor olefin. Reactions of **8** and **1** with styrene or 4-methoxystyrene also gave the same type of spectrum, but it was complicated by the appearance of spectra of other radical species (see further below).

Reactions of **2** or **3** with a styrene where both positions ortho to the vinyl group had been blocked, 2,4,6-trimethylstyrene, did not give spectra of the same appearance as that shown in Figure 2. Instead, about 2 orders of magnitude weaker signals corresponding to several spectra were seen, as exemplified by the reaction of 2,4,6-trimethylstyrene with **3** and **1** (Figure 3). The nature of the radicals corresponding to these spectra was not further elucidated since it was enough to establish the entirely different behavior of a 2,6-disubstituted styrene. Moreover, the task of unambiguously identifying unknown aminoxyl radicals is not a trivial one.

The reaction between **2** and 4-methoxystyrene in chloroform solution in the presence of 5,5-dimethyl-1-pyrroline-*N*-oxide (**9**, DMPO) or 2,4,6-tri(*tert*-butyl)nitrosobenzene (**10**, TTNB), two other commonly used spin traps, was monitored by EPR spectroscopy. No spin adducts were detectable for 50 h in either case.



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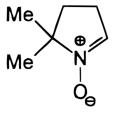
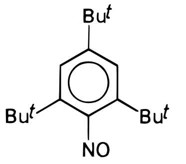


9, DMPO



10, TTNB

Spin Adducts from the Reaction between 8 and 4-Methoxystyrene or Styrene. The trimethyl ester **8** reacted with **1** and 4-methoxystyrene to give a mixed spectrum consisting of three components (Figure 4 and Table 1). The analysis of the small hydrogen coupling constants was performed on the middle group of lines and was partly based on the results of the styrene experiment (see below). The largest component, 82%, had characteristics similar to those of the spectra obtained with **2** or **3**, $a^N = 1.498$, $a^H = 0.217$, $a^{H'} = 0.158$,

Table 1. EPR Spectra Recorded from Reactions between 2, 3, or 8 and Various Styrenes in Chloroform in the Dark

donor olefin	acceptor olefin	a^{N} (mT)	a^{H} (mT)	$a^{H'}$ (mT)	$a^{H''}$ (mT)	$a^{H'''}$ (mT)	%
styrene	**2**	1.486	0.222	0.156	0.052	0.046	
styrene-β,β-d_2	**2**	1.492	0.222	0.024 (D)	0.008 (D)	0.040	
4-F-styrene	**2**	1.482	0.232	0.163	0.053	0.044	
4-MeO-styrene	**2**	1.485	0.212	0.156	0.052	0.046	
4-AcO-styrene	**2**	1.480	0.220	0.156	0.052	0.046	
3-Cl-styrene	**2**	1.484	0.219	0.156	0.052	0.047	
α-methylstyrene	**2**	1.546		0.089	0.038	0.015	
β-methylstyrene	**2**	1.477	0.307		0.047	0.036	
styrene	**3**	1.480	0.210	0.151	0.051	0.047	
styrene-β,β-d_2	**3**	1.486	0.211	0.022 (D)	0.008 (D)	0.047	
4-F-styrene	**3**	1.480	0.215	0.157	0.052	0.046	
4-MeO-styrene	**3**	1.487	0.212	0.156	0.054	0.044	
4-AcO-styrene	**3**	1.480	0.204	0.148	0.054	0.045	
3-Cl−Styrene	**3**	1.475	0.215	0.153	0.054	0.047	
α-methylstyrene	**3**	1.522		0.077			
β-methylstyrene	**3**	1.482	0.268				
4-MeO-styrene	**8**	1.498	0.217	0.158	0.052	0.049	84
		1.413	0.229	0.050	0.018(6)	0.015(3)	15[a]
		1.513	2.03	0.064			1
styrene	**8**	1.497	0.201	0.138	0.057	0.051	47
		1.409	0.231	0.053	0.027(6)	0.022(3)	52[a]
		1.51	2.03	0.068			1

[a] The EPR spectrum of **13** from the reaction between **11** and **8** had $a^{N} = 1.408$, $a^{H} = 0.231$, $a^{H'} = 0.057$, $a^{H''} = 0.023$ (6 H), and $a^{H'''} = 0.029$ (3 H) mT (see text).

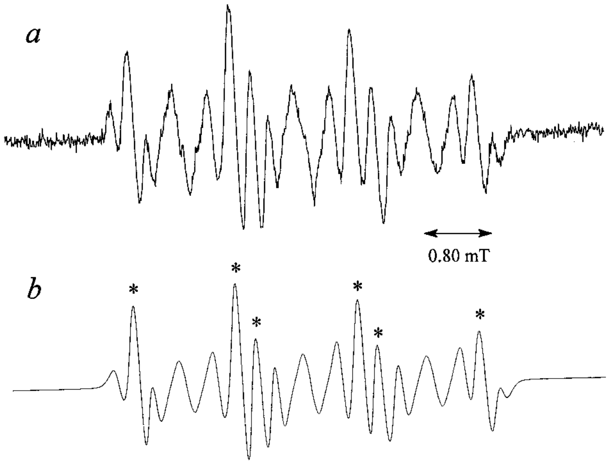


Figure 3. (a) EPR spectrum from a solution of methyl dicyanoacrylate (**3**, 0.25 mol dm^{-3}), 2,4,6-trimethylstyrene (0.20 mol dm^{-3}), and **1** (0.10 mol dm^{-3}) in (^{2}H)chloroform. (b) Simulation based on two spectra with the following parameters: (*, 37%) $a^{N} = 1.466$ and $a^{H} = 1.229$ mT and (63%) $a^{N} = 1.491$, $a^{H} = 0.770$, $a^{H} = 0.425$ (2 H), and $a^{H} = 0.050$ mT.

$a^{H''} = 0.052$, and $a^{H'''} = 0.049$ mT. The second component, 16%, had $a^{N} = 1.413$, $a^{H} = 0.229$, $a^{H'} = 0.050$, $a^{H''} = 0.018$ (6 H), and $a^{H'''} = 0.015$ (3 H) mT, and the third one, 2%, had $a^{N} = 1.513$, $a^{H} = 2.03$, and $a^{H'} = 0.064$ mT.

With styrene, the same three types of spectra were obtained but in different proportions (Figure 5 and Table 1), permitting a reliable dissection and analysis of the spectra of the two major components. The spectrum analogous to the spectra from **2** or **3** in this case constituted 47% of the mixture.

The spectral parameters of the second component (52%) were close to those of the EPR spectrum previously recorded from the dark reaction between α-phenyl-*N*-*tert*-butylnitrone (**11**, PBN) and diethyl fumarate (or maleate) and assigned to what is formally a reductive coupling product (**12**) of **1** and diethyl fumarate. In this reaction, **1** is formed from **11** and the acceptor olefin in a mechanistically not entirely clarified way.[13,14]

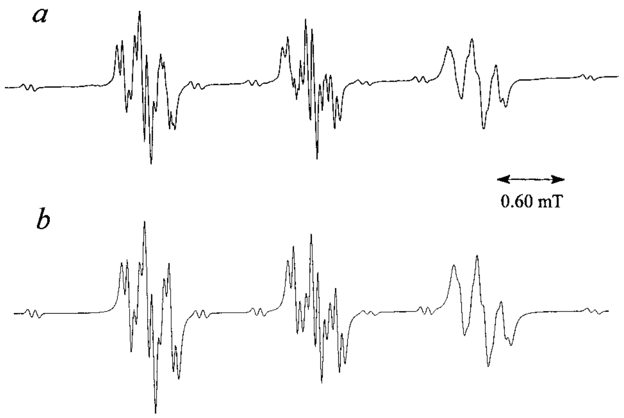
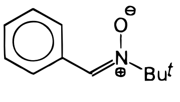
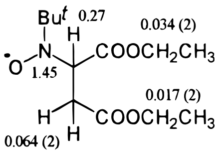


Figure 4. (a) EPR spectrum from a solution of **8** (0.25 mol dm^{-3}), 4-methoxystyrene (0.20 mol dm^{-3}), and **1** (0.10 mol dm^{-3}) in (^{2}H)chloroform. (b) Simulation based on the parameters given in Table 1.

To test if this relationship was correct, the dark reaction between **11** and **8** in chloroform was monitored by EPR spectroscopy. After 20 h, a spectrum with $a^{N} = 1.408$, $a^{H} = 0.231$, $a^{H'} = 0.057$, $a^{H''} = 0.023$ (6 H), and $a^{H'''} = 0.029$ (3 H) mT had developed. It persisted for at least 120 h. The coupling constants are almost identical to those obtained in the **1**−styrene−**8** experiment. Thus, we assign this spectrum to species **13**. The possible genesis of EPR spectra of species such as **12** and **13** from the appropriate activated olefin and **11** is the subject of a separate study.[14]



11, PBN



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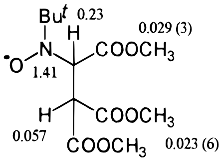


13

The third spectrum (1%) detected is characterized by a large hydrogen coupling of about 2 mT. Similar

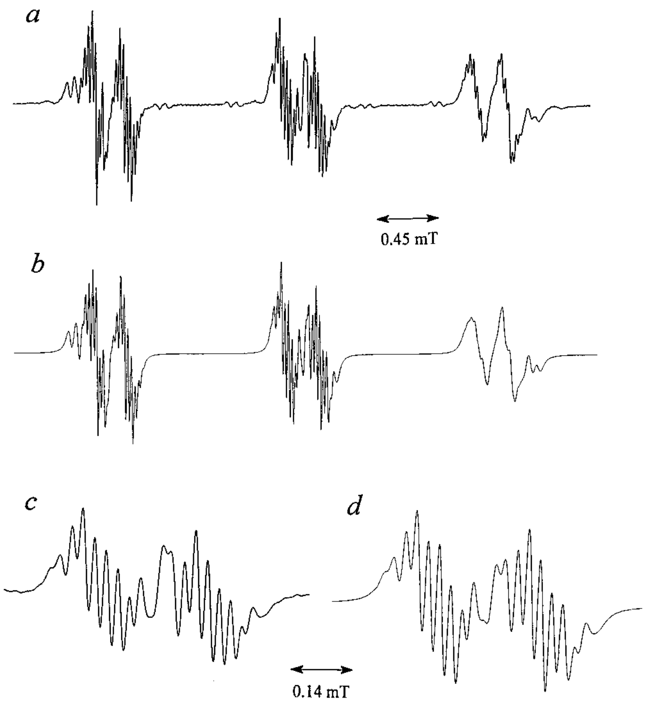
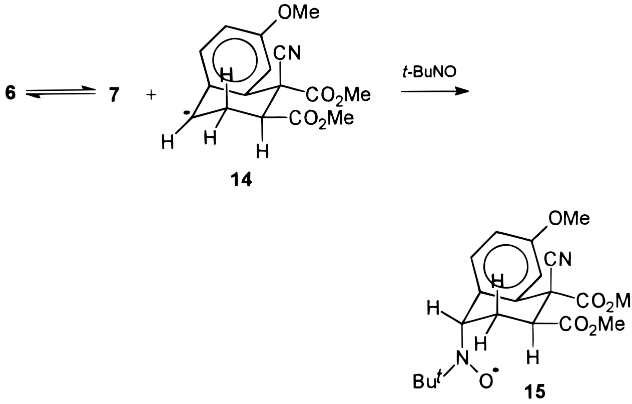


Figure 5. (a) EPR spectrum from a solution of **8** (0.25 mol dm^{-3}), styrene (0.20 mol dm^{-3}), and **1** (0.10 mol dm^{-3}) in (^{2}H)-chloroform. (b) Simulation of spectrum from part a on the basis of the parameters given in Table 1. (c) EPR spectrum of the middle group of lines. (d) Simulation of spectrum from part c on the basis of the parameters given in Table 1.

Scheme 3. Exchange of Radical Traps



spectra have been detected before in reactions between **1** and a mixture of a donor and an acceptor olefin.[8−10] Eventually, it was found that its origin lies in a reaction between **1** and the donor olefin alone.[11,13]

Exchange of the Aminoxyl Group of 6 against 1. **6** is a hydroxylamine which should easily undergo homolysis of the NO−C bond, in analogy to recently developed polymerization initiators of this type.[15] It might then be possible to trap the tetrahydronaphthalenyl radical **14** by **1** and establish the relationship between the spin adduct **15** formed and the one formed and described above from the reaction between **2**, 4-methoxystyrene, and **1** (Scheme 3). In addition, other spin traps might be employed, even if no aminoxyls could be detected in the reaction between 4-methoxystyrene and **1**, **9**, or **10**.

A 5 mmol dm^{-3} solution of **6** in chloroform immediately showed a weak EPR spectrum, in all respects nearly identical with the known spectrum of **7** (see Experimental Section). The spectrum was monitored on a sample kept in the dark for 50 h and showed unchanged intensity during this period (Figure 6, triangles). At this time, **1** (about 4 mmol dm^{-3}) was added. Further monitoring demonstrated an increase in radical concentration, and the signal of **7** was now accompanied by a spectrum with $a^{N} = 1.485$, $a^{H} = 0.212$, $a^{H'} = 0.156$, $a^{H''} = 0.052$ G, and $a^{H'''} = 0.046$ mT, identical (see Table 1) with the spectrum obtained from the reaction between **2**, 4-methoxystyrene, and **1**. This mixture of spectra continued to grow for at least 150 h.

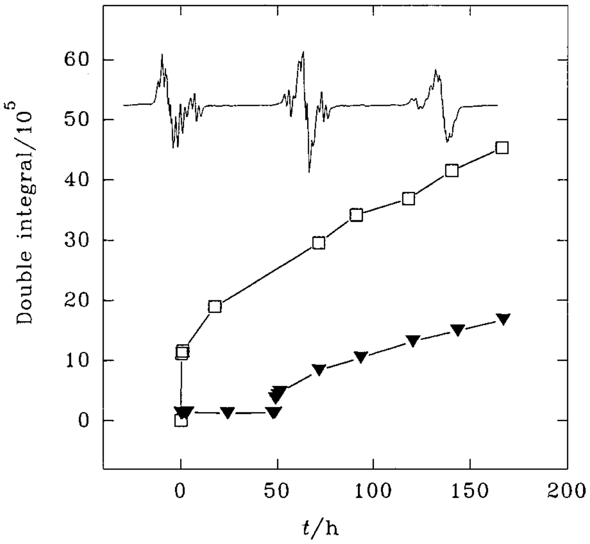


Figure 6. Time development of the EPR spectral intensity (obtained by double integration of the middle group of peaks) from a solution of **6** (5 mmol dm^{-3}) and **1** (about 4 mmol dm^{-3}). **1** was either added after ca. 50 h (triangles) or was present from the beginning (squares; this solution was kept at 45 °C for 10 min). The EPR spectrum shown was recorded after 72 h and represented 52% of **7**.

Next, **1** (about 4 mmol dm^{-3}) was added from the beginning to a 5 mmol dm^{-3} solution of **6**. The solution was kept at 45 °C for 10 min, after which time the same spectral mixture as above had developed at a 10 times higher concentration level (Figure 6, squares). The radical concentration continued to grow for at least 150 h. Figure 7 shows the time development of the two separate radical concentrations from the two experiments.

To check the photosensitivity of **6**, a 5 mmol dm^{-3} solution in chloroform was irradiated by light of $\lambda > 400$ nm. After 10 min of irradiation, the **7** signal had increased by a factor of 10 compared to the dark experiment.

A spin trapping experiment with **6**, using **9** as the spin trap and with benzene as the solvent, showed no indication of spin adduct formation in the dark. Irradiation by light of $\lambda > 400$ nm gave rise to a spin adduct spectrum typical of **9** with $a^{N} = 1.43$, $a^{H} = 2.15$, and $a^{H'} = 0.064$ mT in addition to the **7** spectrum.

With **10** as the spin trap in chloroform, a very weak spectrum with barely recognizable features was obtained from **6** in the dark. In benzene, a composite spectrum of three paramagnetic species developed slowly and was monitored over a period of 5−6 days. After about 50 h, the dominant spectrum was that of **7** [$a^{N} = 1.566$ and $a^{H} = 0.020$ (12 H), 0.042 (4 H), 0.027 (2 H) mT, 55%]. One of the remaining spectra was that expected for a spin adduct in which a radical had been attached to the nitrogen of **10**, *g* being normal for a

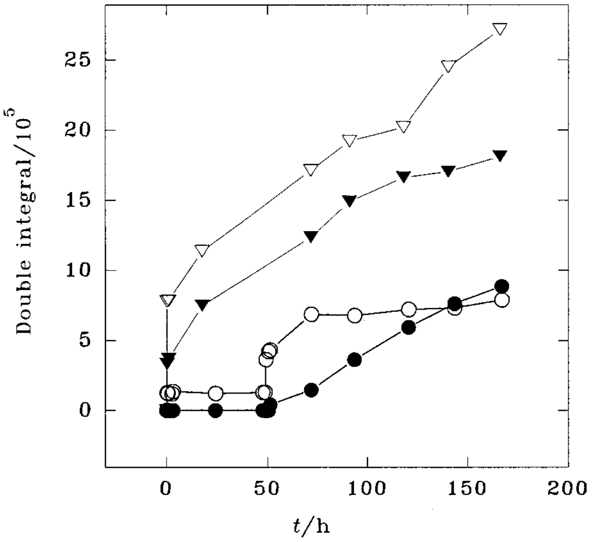


Figure 7. Time development of the EPR spectral intensity (obtained by double integration of the middle group of peaks) of each of the two radicals present in the experiment of Figure 6. Empty symbols represent **7**.

nitroso spin adduct at ca. 2.006, $a^N = 1.36$ and $a^H = 1.53$, 0.080 (3 H) mT, 29%. The third spectrum had a significantly lower g at 2.004, $a^N = 1.07$ and $a^H = 0.170$ (3 H) mT, 16%, typical of *N*-alkoxyanilino radicals formed by trapping at the oxygen of **10**.[16] After 120 h, the proportion between the spectra was 72:21:6, reflecting the lower stability of *N*-alkoxyanilino radicals.

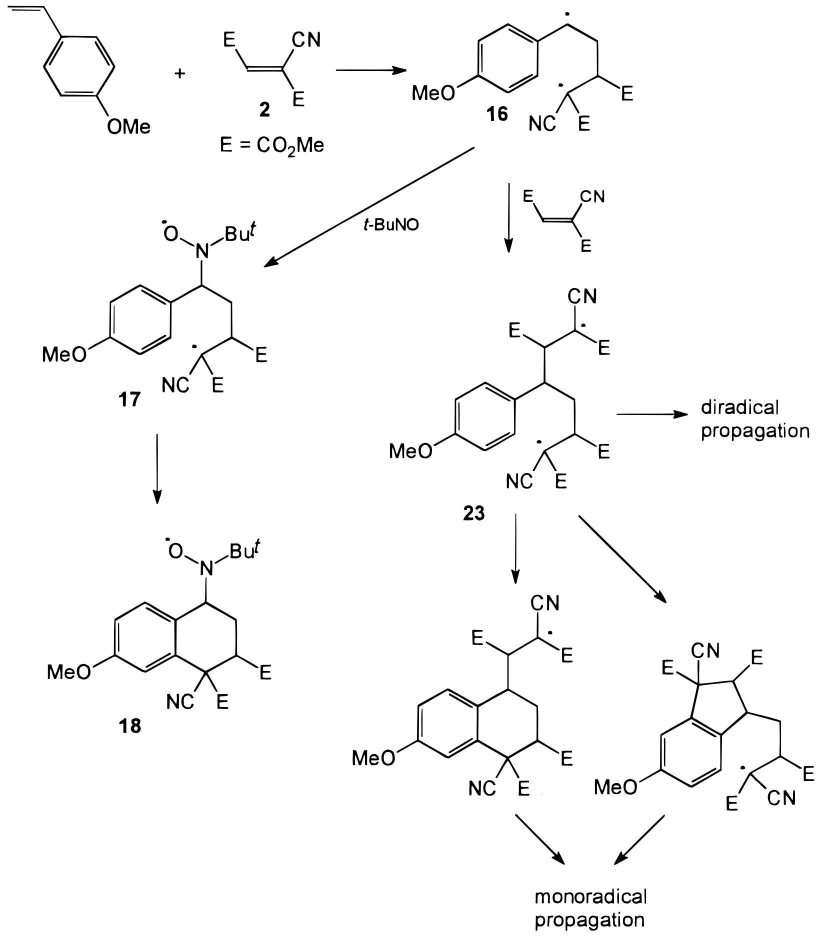
Discussion

Formation and Dissociation of 6. The reaction of **2**, 4-methoxystyrene, and **7** gave a 23% isolated yield of **6**,[5a] now fully characterized by X-ray crystallography. The original NMR spectral assignment of the **7** and cyano substituents being located in axial positions was also found in the solid-state structure of **6** (Figure 1).

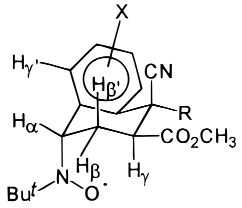
A solution of **6** displayed a weak EPR spectrum of **7** which persisted at the same concentration level (on the order of micromolar) for a long time under dark conditions. Irradiation by light of $\lambda > 400$ nm rapidly increased the **7** concentration. This behavior shows that **6** undergoes a slow thermal dissociation to give **7** and radical **14** (Scheme 3). The reaction can also be photolytically induced. Since **14** is not detected by EPR spectroscopy, it must decay into diamagnetic products in fast reactions. The presence of **14** can be indirectly monitored by trapping it with spin traps (see below).

Formation of Aminoxyls from 2 or 3, Styrenes, and 1. High concentrations of aminoxyls were detected soon after mixing of **2** or **3**, **1**, and a styrene with unsubstituted ortho positions. By analogy with Scheme 1 and as exemplified by the reaction between 4-methoxystyrene, **2**, and **1** in Scheme 4, the diradical first formed (**16**) will react with **1** at the most reactive position derived from the styrene to give radical **17** which undergoes cyclization-oxidation to give aminoxyl **18**. This is a spin adduct which in the case of a styrene with no other substituents at the olefinic system will have five hydrogen atoms, labeled α, β, β', γ, and γ', potentially capable of coupling with the electron spin,

Scheme 4. Reaction of 4-Methoxystyrene with 2 in the Presence or Absence of Radical Trapping Agent



as shown in formula **19**.



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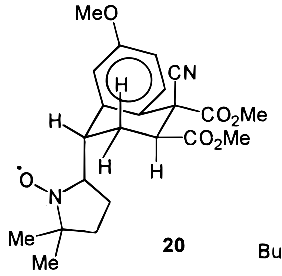
The spectra observed have four distinguishable hydrogen couplings, the largest one (ca. 0.2 mT) being assigned to H_α. The next largest one (about 0.16 mT) is assigned to the equatorial H_β since in this position the C−H bond will be almost parallel to the π orbitals of the N−O$^\bullet$ system.[17] The coupling of about 0.05 mT is assigned to the axial $H_{\beta'}$ and the smallest coupling to either H_γ or $H_{\gamma'}$.

The spectra obtained with styrenes substituted at the double bond agree with the connectivity of **18**. The use of β,β-bisdeuterated styrene affected H_β and $H_{\beta'}$, whereas the use of α- or β-methylstyrene removed the coupling to H_α or H_β, respectively. When both ortho positions of the styrene were blocked by methyl groups, the EPR spectra of the radicals detected (Figure 3) were quantitatively and qualitatively entirely different, in line with the requirement that the formation of **18** needs at least one unsubstituted ortho position. We will not further elaborate on the possible nature of the radicals obtained from 2,4,6-trimethylstyrene in view of the complicated chemistry involved in reactions between nitroso compounds and olefins.[11,18]

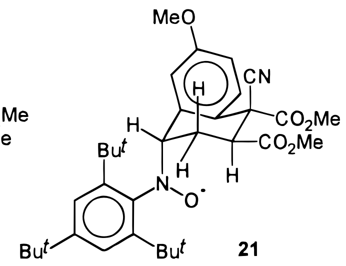
Formation of Aminoxyls from 8, Styrenes, and 1. In principle, the acceptor olefin **8** gave the same reaction with **1** and a styrene as **2** or **3**. However, the simultaneous appearance of (i) the spectrum of **13** and (ii) a spectrum with a very large hydrogen coupling (about 2 mT) detected earlier in spin trapping studies of polymerization[9,10,11] made **8** less attractive from the present point of view, and therefore only two styrenes were investigated.

Formation of 15 from 6. As shown in Scheme 2, the fact that **6** dissociates into **7** and a radical **14** provided the possibility of establishing the connection between **6** and **15** by trapping **14** with **1**. These experiments demonstrated clearly that **15** formed from a solution of **6** and **1** was identical to that formed from **2**, 4-methoxystyrene, and **1**. The use of two other spin traps, **9** and **10**, also provided spin adducts **20**−**22** in benzene with the characteristics expected. The use of benzene gave higher concentration of radicals, as is common in spin trapping chemistry. The fact that no spin adducts were detected in solutions of **2**, 4-methoxystyrene, and **9** or **10** is probably due to the lower reactivity of **9** and **10** toward radicals in comparison to **1**.[17]

Relevance to Spontaneous Initiation of Copolymerization. The results above demonstrate that, in the reaction between a donor styrene-type olefin and an acceptor olefin, a bond is formed between the β-carbons of the two olefins leading to an intermediate tetramethylene diradical. In this proposed diradical, the reactive electron-rich benzylic radical reacts first with the trapping agent, after which the electron-poor, more stabilized radical end will attack the aromatic ring. H atom transfer will give rise to trapping products similar to **6**, observed by isolation or by EPR spectroscopy.



20



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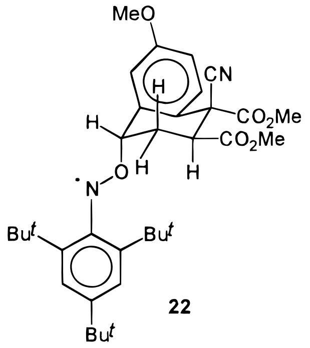

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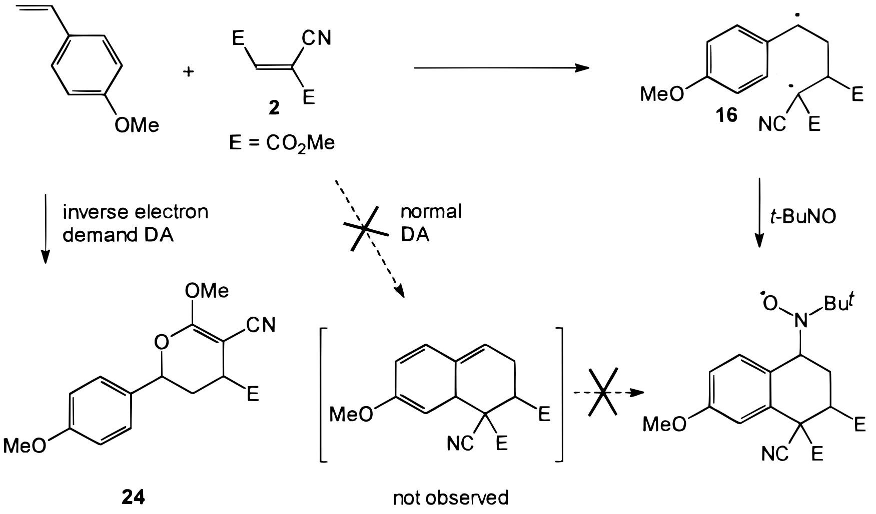
The next question is as follows: what happens in polymerization conditions in the absence of a trapping reagent? The moderately stabilized, electron-rich benzylic radical center can react very rapidly with another molecule of electron-poor olefin to form a second strongly stabilized, electron-poor radical center. This extended diradical **23** can initiate alternating copolymerization (Scheme 4). Addition of electron-rich styrene monomer is energetically uphill and probably reverse depropagation of this step would occur, were it not that another electron-poor molecule catches it and drives the reaction forward.

This above sequence of events is idealized. From this study, other reaction pathways are possible. Cyclization into the electron-rich aromatic ring from extended diradical **23** may occur from either electron-poor end, as shown in Scheme 4, leading either to a five- or six-membered ring. Subsequent H atom transfer can then form two *mono* radicals. Either one of these pathways might give a monoradical contribution to the diradical propagation.

A Mayo-type initiation mechanism, in which initial formation of a Diels−Alder cycloadduct is followed by H atom transfer to another monomer (MAH, molecule assisted homolysis), can be discounted in this case. No evidence can be found in the literature for any other case of MAH for such cycloadducts. However, very recently Scaiano et al.[19] have demonstrated the existence of a diradical, namely the 1,4-diphenyl-1,4-butanediyl diradical, which among other products leads to 1-phenyl-1,2,3,4-tetrahydronaphthalene, the same adducts as proposed by the Mayo mechanism. As our earlier investigations and others have shown, normal Diels−Alder reactions into the ring, when they do occur, are immediately followed by either an ene reaction or a second Diels−Alder reaction with an additional molecule of the electron-poor olefin.[20,21,12b] No such 1:2 adducts have been encountered in the present cases. Also, inverse electron-demand Diels−Alder cycloaddition to form a pyran adduct **24** is already observed in the systems of 4-methoxystyrene with **2** or **3**, in which the electron-poor olefin provides the heterodiene and the styrene acts as the dienophile (Scheme 5). It seems very unlikely that inverse and normal Diels−Alder reactions

Scheme 5. Mayo Cycloadduct Is Not Formed



of the same two reagents could occur at comparable rates.

6 is an alkoxyamine of a type similar to those recently developed for living free radical polymerizations.[15] These initiators are normally used at temperatures around 120 °C and then have half-lives of 5−10 min, and it is therefore pertinent to ask if the homolytic cleavage reaction of **6** in Scheme 3 can be feasible at room temperature. The first-order rate constant for growth of spin adduct **15** (as calculated from Figure 7, curve with filled circles, in the region of 50−170 h) is approximately 4×10^{-5} min^{-1}, equal to a half-life of about 300 h at room temperature. Considering also the fact that **15** has an activating 4-methoxy group, the two time scales are reasonably well consistent.

Conclusions

The results described and discussed above show that a trisubstituted acceptor olefin reacts with a phenyl-substituted donor olefin to give a diradical with significant difference in reactivity between the radical centers. This makes possible trapping of the more reactive center by **1** and subsequent reaction of the less reactive center by cyclization into the phenyl group followed by H atom transfer. As far as the initiation of spontaneous polymerization of electron-rich styrene with electrophilic olefins is concerned, all of our results are completely consistent with initial formation of a polar tetramethylene diradical. The ensuing reactions are also explained in terms of electron-rich/-poor character. No evidence supporting a Mayo mechanism, electron transfer, or charge-transfer complex initiation was found.

Experimental Section

Materials. The spin traps, **1** and **9**−**11**, were purchased from Aldrich or Lancaster, as were the styrene derivatives used, except for styrene-β,β-(^{2}H$_2$), which was obtained from Dr. Glaser AG, Switzerland. **2**, **3**, and **8** were available from earlier studies.[5] **6** was prepared according to a published method.[12a] (^{2}H)Chloroform was from Dr. Glaser AG, Switzerland.

EPR Spectroscopy. EPR spectra were recorded by the upgrade version ESP 3220−200SH of a Bruker ER-200D spectrometer. The EPR measurements were made using a 100 kHz modulation frequency, a microwave effect of 0.4−1.25 mW, and a modulation amplitude of 0.01−0.04 mT. Simulations were carried out by the public domain program WINSIM.

X-ray Crystallography. Intensity data for **6** were collected with a Siemens SMART CCD area detector using monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. The crystal used was a colorless block of dimensions $0.61 \times 0.45 \times 0.36$ mm^3 and was obtained by slow evaporation, at −4 °C, of a solution of **6** in diethyl ether. A total of 17 942 reflections were collected which, after merging ($R_{\mathrm{int}} = 0.0428$), gave 5025 unique reflections (99.6% completeness). The intensities were corrected for Lorentz and polarization effects and for absorption ($T_{\max} = 0.969$, $T_{\min} = 0.948$).

The structure was solved by direct methods using *SHELXS90*[22] and refined on F^2 by unrestrained full-matrix least-squares procedures using *SHELXL-96*.[23] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were included in calculated positions with isotropic displacement coefficients equal to 1.2 times the isotropic equivalent of their carrier carbons. The function minimized was $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.0635P^2]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. A final difference map showed no features greater or less than 0.25 e$^-$/Å^3.

Crystal Data at −120 °C. C$_{25}$H$_{34}$N$_2$O$_6$: $M_r = 458.54$; monoclinic; space group $P2_1/c$; $a = 8.369(2)$, $b = 24.434(5)$, and $c = 12.512(3)$ Å; $U = 2456.7(9)$ Å^3; $F(000) = 984$; $Z = 4$; $D_c = 1.240$ g cm^{-3}; μ(Mo−Kα) = 0.088 mm^{-1}; $2\theta_{\max} = 53°$; 300 parameters; $wR_2 = 0.1139$ for all 5025 data; $R_1 = 0.0442$ for 3367 data with $F_o > 4\sigma(F_o)$.

Reaction between an Acceptor and a Donor Olefin and 1. Weighed or pipetted amounts of **1**, acceptor, and donor olefin in (^{2}H)chloroform (700 μl, stabilized by silver foil; used in order to avoid contamination by the ethanol present in ordinary chloroform) was introduced into an EPR tube. After being degassed with argon for 2 min, the tube was sealed and the EPR spectral recording was started. The sample preparation was performed in a semidarkened room, and the sample tube was stored in complete darkness outside the measurement periods.

Reaction between 6 and 1. **6** (5 mmol dm^{-3}) in (^{2}H)-chloroform immediately gave rise to a weak EPR spectrum of **7** ($a^{\mathrm{N}} = 1.598$, $a^{\mathrm{H}} = 0.017$ (12 H), $a^{\mathrm{H}} = 0.043$ (4 H), and $a^{\mathrm{H}} = 0.022$ (2 H) mT; lit.[24] $a^{\mathrm{N}} = 1.606$, $a^{\mathrm{H}} = 0.022$ (12 H), $a^{\mathrm{H}} = 0.039$ (4 H), and $a^{\mathrm{H}} = 0.018$ (2 H) mT). The concentration of **7** was approximately constant at the 1 μmol dm^{-3} level for 50 h, after which time **1** (ca. 4 mmol dm^{-3}) was added. The concentration of **7** rapidly increased and a new spectrum developed (Figures 6 and 7).

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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