

# Photochemically- and Thermally-Initiated Decomposition of Hexazadienes

## An EPR and Cyclovoltammetric Study

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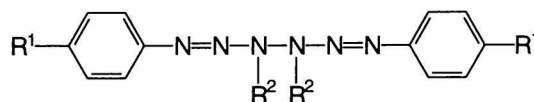
The investigated  $R^1-C_6H_4-N_2-NR^2-NR^2-N_2-C_6H_4-R^1$  hexazadienes with  $R^1 = Cl, COCH_3, COOCH_2CH_3$  and  $R^2 = COCH_3$  and  $CH_3$  are characterized by cyclic voltammetry in acetonitrile solutions with an irreversible reduction wave in the potential range from  $-1.7$  V to  $-2.0$  V vs. saturated calomel electrode (SCE). After cathodic reduction they decompose under the formation of highly reactive radicals, which are terminated with solvent or support salt. Radicals  $R^1C_6H_4\cdot$ ,  $\cdot CH_2CN$ , and  $\cdot CHXCH_2CH_2CH_3$  were found using spin trap technique. Upon irradiation under day-light and still more upon UV irradiation, hexazadienes decompose in  $CH_3CN$  solution in a few seconds and form primarily  $R^1C_6H_4\cdot$ ,  $\cdot CH_2CN$  and finally  $\cdot CH_3$  adducts to nitrosodurene (ND). Under thermally-initiated decomposition  $R^1C_6H_4\cdot$  and  $\cdot H$  adducts to ND were observed at 350 K.

Hexazadienes are azo analogous compounds containing six nitrogen atoms in a linear chain. The hexaza-1,5-dienes ( $R^1-C_6H_4-N_2-NR^2-NR^2-N_2-C_6H_4-R^1$ ) investigated here can be synthesized *via* two routes: *a*) *In situ* coupling of two triazenyl radicals [ $R^1-N=N-\dot{N}-R^2$ ] which are generated by the oxidation of the corresponding triazenes ( $R^1-N=N-NHR^2$ ) [1, 2] or *b*) by coupling of two diazonium equivalents [ $R^1-N\equiv N^+$ ] with one equivalent of hydrazine derivatives [3]. Similarly to triazenes, hexazadienes also show very limited photochemical stability due to the high content of elementary nitrogen (up to 30 %). In addition, they are highly thermally labile [4]. The decomposition of the closely related triazenyls has already attracted considerable attention [5]. The mechanically- [2], thermally- [1–7], and chemically-induced [7] decomposition of hexazadienes has been reported. Their photolysis and thermolysis have been studied in more detail in [4]. The present paper expands this study to include EPR investigations of the radical products formed in the electrochemically-, photochemically-, and thermally-initiated decomposition of the hexazadiene compounds listed in Table 1.

### EXPERIMENTAL

The hexazadienes I–IV (Table 1) were prepared as described in [4]. The spin trap nitrosodurene (ND) was obtained from OMRF, Oklahoma,

**Table 1.** The Investigated Hexazadiene Compounds and Their Cyclo-voltammetric Data (Cathodic Peak Potential  $\bar{E}_{pc}$ , Degree of Reversibility  $D_r$ ) Measured in 0.001 M of Sample, and 0.1 M-TBAP in Acetonitrile Solutions



Sample	$R^1$	$R^2$	$-\bar{E}_{pc}/V$	$D_r$	$\bar{E}_{pc}/V$
I	Cl	COMe	1.70	irrev.	0.11
			1.92	irrev.	
			1.25	irrev.	
II	Cl	Me	$\approx 2$	irrev.	–
III	COMe	Me	1.83	irrev.	(–0.89)
					0.17
IV	COOEt	Me	1.71	irrev.	(–1.04)
					0.17

USA, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), 2-methyl-2-nitrosopropane (*t*-BuNO), and support salt tetrabutylammonium perchlorate (TBAP) were from Sigma, and acetonitrile (ACN) and benzene of anal. grade were commercial products from Fluka.

Electrochemical investigations were carried out in

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ACN containing the investigated substrate ( $c = 10^{-3}$  mol dm $^{-3}$ ) and TBAP ( $c = 10^{-1}$  mol dm $^{-3}$ ) under an argon atmosphere. The cyclic voltammetric experiments were performed with a PAR 270 instrument using a three-electrode system involving platinum working and auxiliary electrodes and a reference saturated calomel electrode (SCE). *In situ* electrochemical EPR measurements were carried out in a Varian cell.

The photochemical as well as the thermal investigations were also performed directly in the cavity of EPR spectrometer using a 250 W medium-pressure mercury lamp (from Applied Photophysics, UK) as the irradiation source, and a Bruker Variable Temperature Unit, respectively. To measure and to simulate the obtained EPR spectra, a Bruker spectrometer 200D working in X-band equipped with the Aspect 2000 computer was used.

The very limited photochemical as well as thermal stability of hexazadienes presents a serious experimental problem. Therefore, the samples were mostly prepared in the dark or directly in the cavity of EPR spectrometer or CV cell. In most cases prior formation of radicals was eliminated or substantially minimized.

## RESULTS AND DISCUSSION

### Electrochemical Investigation

*Cyclic voltammetry:* The data obtained in the cathodic reduction of the investigated compounds, as cathodic ( $\overline{E}_{pc}$ ) and reverse cathodic ( $\overline{E}_{pc}$ ) peak potential with the corresponding degree of reversibility are summarized in Table 1. Fig. 1 represents a characteristic cyclic voltammogram of 3,4-dimethylhexadienes obtained using compound III.

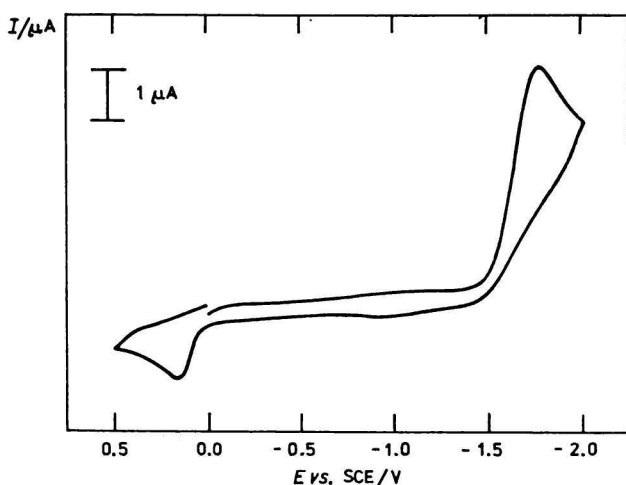


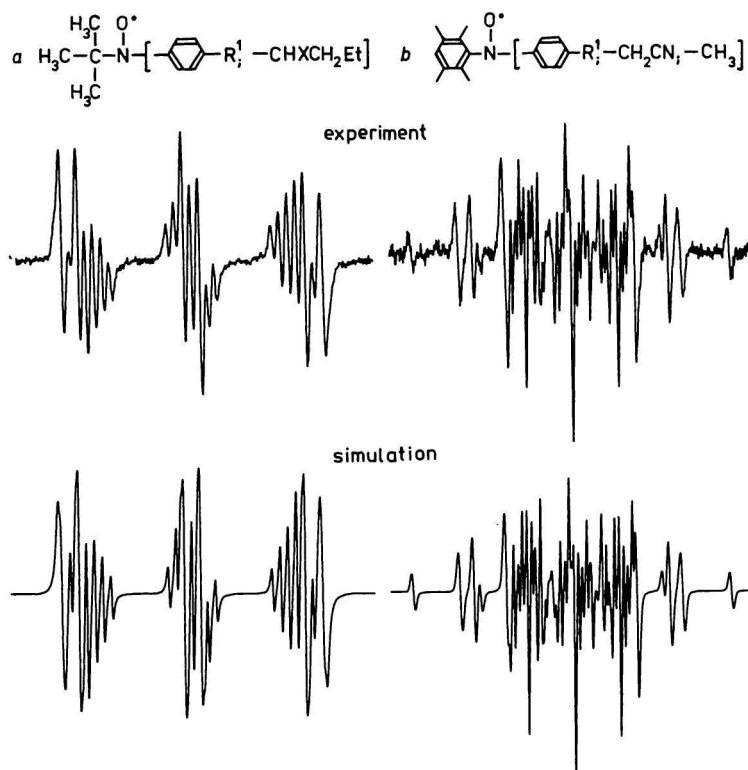
Fig. 1. Cyclic voltammogram obtained from 0.001 M-probe III and 0.1 M-TBAP in acetonitrile solution with a scan rate of 500 mV s $^{-1}$ .

Characteristic of all the investigated hexazadienes is one irreversible reduction wave in the potential range from  $-1.7$  V to  $-2$  V. It has a shape and cyclic voltammetric characteristic similar to those found in the case of triazenes. Therefore the most likely step here is the reduction of the azo group in the triazene arrangement of hexazadienes. Only compound I showed an additional, second reduction wave in this region ( $-1.7$  V and  $-1.92$  V). Its origin is not obvious. The reduction of the carbonyl group is a plausible alternative. The third reduction wave at  $-1.25$  V quoted in Table 1 was increasingly observed after several scans and it obviously belongs to the splitting products formed by further decomposition of triazene unit (photochemical splitting cannot be fully excluded). On the reverse scan a consecutive product in the region of 0.1 V is evident for compounds I, III, IV. A clear evidence for it is missing in the case of compound II. Additionally compounds III and IV showed less pronounced reverse peaks at  $-0.89$  V and  $-1.04$  V, respectively.

This cyclic voltammetric behaviour of hexazadienes suggests their electrochemically-initiated decomposition. Consequently, their cathodic reduction was investigated by EPR spectroscopy.

*EPR investigation:* In accord with the high degree of irreversibility found in the cyclic voltammetric experiment, no stable radicals were observed by means of EPR technique in *in situ* cathodic reduction. Therefore further investigations were carried out in the presence of spin trap.

Using *t*-BuNO, complex superimposed spectra were observed even before electrolysis by all samples in ACN solution with TBAP as support electrolyte (a representative result is shown in Fig. 2a for compound IV). The splitting constants extracted by the simulation and the measured *g*-values of radicals are summarized in Table 2. Two types of radicals are evident in the spectra (Fig. 2a). The direct product of the hexazadiene splitting is represented by the corresponding substituted phenyl radical: *p*-Cl-C $_6$ H $_4$  ( $a_1$ ) from compounds I and II, *p*-MeOC-C $_6$ H $_4$  observed for compound III, and *p*-EtOOC-C $_6$ H $_4$  for compound IV ( $b_1$ ) with splitting constants as quoted in Table 2. The second radical,  $\cdot$ CHXCH $_2$ CH $_2$ CH $_3$  ( $f$ ), is an adduct originating from the *n*-butyl group of TBAP salt, already found before [8] in the cathodic reduction of azo compounds. (Reactive radicals formed in the decomposition attack the tetrabutylammonium cation and the thus modified *n*-butyl group is added to the spin trap.) From the splitting constants  $a_N(\text{NO}) = 1.478$  mT,  $a_H(\text{CH}) = 0.21$  mT, and  $a_H(\text{CH}_2) = 0.03$  mT employed in the simulation, methylene protons with  $a_H(\text{CH}_2) = 0.03$  mT were not clearly evident in the hyperfine structure of the spectrum, but it was necessary to consider them by the simulation to fit the line shape of the experimental spectra.



**Fig. 2.** Experimental and simulated spectra observed a) by the cathodic reduction of acetonitrile solution of compound *IV* in the presence of *t*-BuNO spin trap and b) by the photolysis of compound *III* in ACN employing ND spin trap.

**Table 2.** Splitting Constants of Radicals Obtained by Electrochemically- ( $+e^-$ ), Photochemically- (irr.), and Thermally- (T) Initiated Decomposition of Hexazadienes

Radical	Structure	Splitting constant/mT			<i>g</i> -Value	Spin trap	Method/Probe	
<i>a</i> <sub>1</sub>		<i>a</i> <sub>N</sub> (NO)	1.25	<i>a</i> <sub>H</sub> ( <i>m, m</i> )	0.100	2.0057	<i>t</i> -BuNO	$+e^-$ / I, II
		<i>a</i> <sub>H</sub> ( <i>o, o</i> )	0.287	<i>a</i> <sub>Cl</sub>	0.031			
<i>a</i> <sub>2</sub>		<i>a</i> <sub>N</sub> (NO)	0.993	<i>a</i> <sub>H</sub> ( <i>m, m</i> )	0.098	2.0057	ND	irr., T / I, II
		<i>a</i> <sub>H</sub> ( <i>o, o</i> )	0.276	<i>a</i> <sub>Cl</sub>	0.030			
<i>b</i> <sub>1</sub>		<i>a</i> <sub>N</sub> (NO)	1.275	<i>a</i> <sub>H</sub> ( <i>m, m</i> )	0.096	2.0058	<i>t</i> -BuNO	$+e^-$ / III, IV
		<i>a</i> <sub>H</sub> ( <i>o, o</i> )	0.272					
<i>b</i> <sub>2</sub>		<i>a</i> <sub>N</sub> (NO)	0.967	<i>a</i> <sub>H</sub> ( <i>m, m</i> )	0.097	2.0058	ND	irr., T / III, IV
		<i>a</i> <sub>H</sub> ( <i>o, o</i> )	0.278					
<i>c</i>	H <sub>3</sub> C <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.410	<i>a</i> <sub>H</sub> (CH <sub>3</sub> )	1.277	2.0060	ND	irr. / II, III, IV
<i>d</i>	?	<i>a</i> <sub>N</sub> (NO)	2.811			2.0062	ND	irr. / I
<i>e</i>	C <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.398	<i>a</i> <sub>H</sub>	2.120	2.0059	DMPO	irr. / I, II, III, IV
<i>f</i>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> XHC <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.478	<i>a</i> <sub>H</sub> (CH)	0.210	2.0067	<i>t</i> -BuNO	$+e^-$ / I, II, III, IV
				<i>a</i> <sub>H</sub> (CH <sub>2</sub> )	0.030			
<i>g</i>	NCH <sub>2</sub> C <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.390	<i>a</i> <sub>H</sub> (CH <sub>2</sub> )	0.946	2.0062	ND	irr. / I, II, III, IV
<i>h</i>	H <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.426	<i>a</i> <sub>H</sub>	1.367	2.0059	ND	T / I, II, III, IV
<i>i</i>	D <sup>•</sup>	<i>a</i> <sub>N</sub> (NO)	1.426	<i>a</i> <sub>D</sub>	0.210	2.0059	ND	T / I, II, III, IV

### Photochemical Initiation

Due to the instability of hexazadiene radical products, no EPR response was obtained in their direct photolysis in the EPR spectrometer. Consequently, further measurements were performed in the presence of ND and DMPO spin traps in ACN solution.

3,4-Diacetyl hexazadiene (*I*) was the only com-

pound not giving the radical adduct prior to the photolysis. After 1 s of irradiation, *p*-Cl—C<sub>6</sub>H<sub>4</sub>—ND<sup>•</sup> adduct with the splitting constants *a*<sub>H</sub>(*m, m*) = 0.098 mT, *a*<sub>H</sub>(*o, o*) = 0.276 mT, *a*<sub>Cl</sub> = 0.030 mT, *a*<sub>N</sub>(NO) = 0.993 mT and *g*-value 2.0057 was found (Table 2, *a*<sub>2</sub>). This tends to indicate that the primary step in hexazadiene decomposition is the splitting of the azo group. Then, after further 3 s of irradiation a new type

of adduct, without contribution to the hyperfine structure, represented in the spectrum by triplet (1:1:1), was formed, simulated with splitting constant  $a_N = 2.811$  mT (Table 2, *d*). Its  $g$ -value was 2.0062 and it had a very limited stability after stopping the irradiation. These are characteristic properties of oxygen-centred radicals ( $RO^\bullet$ ). In the case of hexazadiene *I* only acetyl group contains oxygen. The formation of an alkoxy radical in this system is not clear at present. This sequence of radical products implies that in the secondary step the hydrazo skeleton is splitted. Fig. 2*b* shows the characteristic EPR spectra generally found in the photochemical decomposition of 3,4-dimethyl hexazadienes (*II–IV*) using compound *III*. In complex superimposed spectra two types of adducts were found even before the photolysis: namely, that of *para*-substituted phenyl radical (Table 2, *b*<sub>2</sub>) formed by the splitting of the parent hexazadiene structure and  $CH_2CN-ND^\bullet$  (Table 2, *g*) and the second adduct originating from the solvent after H abstraction. This is due to the termination of the reactive intermediates formed during decomposition of 3,4-dimethyl hexazadiene. In the advanced photolysis the third type of radical was formed (Table 2, *c*), confirming the splitting of methyl group from hexazadiene skeleton. All these three adducts are evident from the simulation of experimental spectra shown in Fig. 2*b*. This succession of radical products tends to suggest again that

the hydrazo skeleton is split in the final stage of decomposition.

The radicals found in the photolytic experiment in the presence of ND spin trap were also confirmed by the measurements using DMPO spin trap. All compounds gave a sextet spectrum characteristic of a carbon-centred radical with the splitting constants  $a_N(NO) = 1.398$  mT,  $a_H = 2.12$  mT and  $g$ -value 2.0059 (Table 2, *e*). Only 3,4-dimethyl hexazadienes formed such a carbon-centred radical even before the irradiation, and 3,4-diacetyl hexazadiene formed such an adduct after the first second of irradiation.

### Thermal Decomposition

The high instability of the radicals intermediately formed was also confirmed in the thermal measurements of hexazadienes. Here, the acetonitrile used above as a solvent was replaced with benzene to attain higher temperatures than the boiling point of ACN. In benzene solutions without spin trap, no radicals were observed up to 343 K. Therefore the solutions were warmed up directly in the EPR spectrometer to this temperature with spin trap.

To eliminate the contribution of light to the decomposition of hexazadiene, the solutions were prepared in the dark. The samples were exposed to light only for the time needed to put the cell into the cavity of

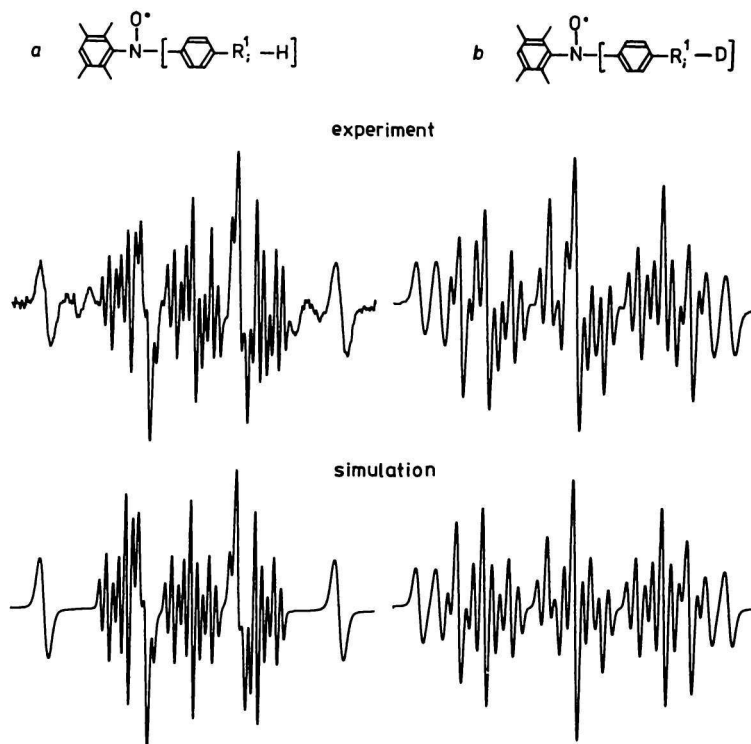


Fig. 3. Experimental and simulated EPR spectra measured by the thermal decomposition of compound *III* in benzene (*a*) and deuterated benzene (*b*) in the presence of ND spin trap.

the spectrometer (3–5 s). Already in this short time the decomposition at the room temperature was evident. The superimposed spectra of  $\cdot\text{ND—H}$  (Table 2, *h*) and  $\cdot\text{ND—C}_6\text{H}_4\text{—}p\text{-(Cl, R}^1\text{)}$  (Table 2, *a*<sub>2</sub> and *b*<sub>2</sub>) adducts were formed at 298 K for all hexazadienes, as shown in Fig. 3*a* using hexazadiene *III*; the splitting constants obtained by their simulation are given in Table 2, *b*<sub>2</sub>. The concentration of these decomposition products changed with the temperature. At 298 K the ND—H adduct prevailed.  $\cdot\text{ND—Ph}$  adduct was increasingly observed at the higher temperatures.

To eliminate the exposure to light completely, the solutions were prepared directly in the cavity of the spectrometer in the cell already purged with argon. Under these conditions for 3,4-diacetyl hexazadiene no radicals were observed below 350 K. At 350 K the *p*-Cl—C<sub>6</sub>H<sub>4</sub>—ND $\cdot$  (Table 2, *a*<sub>2</sub>) adduct was found. For all other 3,4-dimethyl hexazadienes the corresponding substituted phenyl—ND (Table 2, *a*<sub>2</sub> and *b*<sub>2</sub>) adduct was observed already at room temperature, indicating the very high thermal lability of investigated compounds.

The reason for the formation of  $\cdot\text{ND—H}$  adduct is not obvious, as there is no simple way for the hydrogen radical intermediate to form. To specify the origin of the hydrogen we carried out the corresponding experiments in deuterated benzene solvent. The spectrum shown in Fig. 3*b* was obtained; it can be well fitted by simulation replacing the hydrogen splitting constant  $a_{\text{H}} = 1.367$  mT (Table 2, *h*) with the corresponding deuterium parameter  $a_{\text{D}} = 0.21$  mT (Table 2, *i*). This confirms that the hydrogen in the observed  $\cdot\text{ND—H}$  adduct originates from the solvent. It indicates that

benzene solvent participates in a more complex termination reaction than the above-described acetonitrile, where only a direct termination fragment after the H $\cdot$  abstraction ( $\cdot\text{CH}_2\text{CN}$ ) was found. Thus hexazadienes may form  $\text{R}^1\text{C}_6\text{H}_4\text{—N}_2\cdot$  intermediates, which are immediately terminated with benzene solvent to the azo compound  $\text{R}^1\text{C}_6\text{H}_4\text{—N}_2\text{—H}$ . This further decomposes to  $\text{R}^1\text{C}_6\text{H}_4\cdot + \text{N}_2 + \cdot\text{H}$ , and hydrogen thus formed is trapped to the observed  $\cdot\text{ND—H}$  adduct.

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