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Radical Products of the Oxidation of 2,2-Diacyl-1-arylhydrazines with the System $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2

L. Omelka[1,*], **R. Kluge**[2], and **M. Schulz**[2]

[1] Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, SK-81237 Bratislava, Slovakia
[2] Institute of Organic Chemistry, Martin-Luther-University Halle-Wittenberg, D-06217 Merseburg, Federal Republic of Germany

Summary. The oxidation of 2,2-Diacyl-1-arylhydrazines **1a–l** with the system $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2 led to the formation of two types of radical products. Phenazinium cation radicals **5a–h** were formed from 2,2-diacyl-1-arylhydrazines **1a–h**, while hydrazyl radicals **2i–l** were observed to be the only radical products of the oxidation of **1i–l**. The generated radicals are characterized by their EPR parameters.

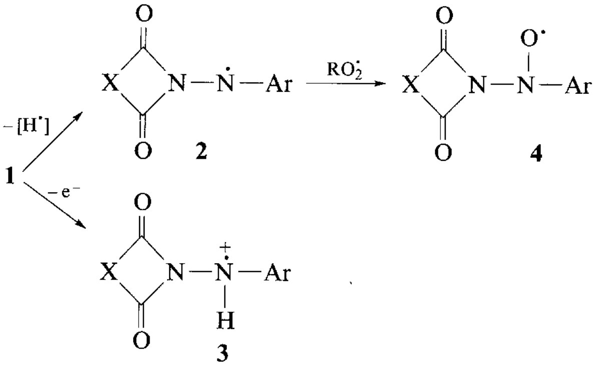
Keywords. 2,2-Diacyl-1-arylhydrazines; EPR; Hydrazyl radicals; Phenazinium cation radicals.

Radikalische Produkte der Oxidation von 2,2-Diacyl-1-arylhydrazinen mit dem System $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2

Zusammenfassung. Die Oxidation der 2,2-Diacyl-1-arylhydrazine **1a–l** mit dem System $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2 führte zu zwei unterschiedlichen Typen von Radikalen. Aus den 2,2-Diacyl-1-arylhydrazinen **1a–h** werden die Phenaziniumkationenradikale **5a–h** gebildet, während nach Oxidation von **1i–l** die entsprechenden Hydrazyle **2i–l** als einzige Radikalprodukte nachweisbar waren. Die erzeugten Radikale wurden durch ihre EPR-Parameter charakterisiert.

Introduction

In previous investigations [1, 2], we dealt with the oxidation of 2,2-Diacyl-1-arylhydrazines (**1**) using various agents (PbO_2, $RO_2^{\cdot}$, dibenzoylperoxide, $Pb(OAc)_4$). The general mechanism outlined in Scheme 1 implies the formation of hydrazyls **2**, hydrazinium cations **3**, and hydrazoxyls **4** in the course of the oxidation reaction. While the occurrence of hydrazyls **2** and cation radicals **3** was deduced from the analysis of the reaction products [1], the hydrazoxyl radicals **4** were detected by EPR spectroscopy in reaction with catalytically generated $RO_2^{\cdot}$ radicals [2]. The subsequent preliminary study of the oxidation of some *tert*-butyl substituted 2,2-diacyl-1-arylhydrazines [3] evidenced the formation of hydrazyl radical **2l** by PbO_2 oxidation of **1l** containing *tert*-butyl groups in positions 2 and 4 of phenyl



Scheme 1

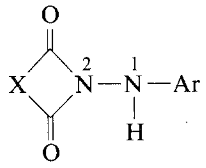
ring. The system Pb(OAc)$_4$–CF$_3$COOH–CH$_2$Cl$_2$ (suggested by *Neugebauer* [4] for the preparation of cation radicals from substituted diphenylamines) was also found to be an effective agent for the generation of neutral and ion radicals. On the basis of these experimental results, we attempted to prepare hydrazyls **2** by the oxidation of **1a–k** with the above mentioned systems. In contrast to **1l**, no radical products were detected when hydrazines **1a–k** were oxidized with PbO$_2$ in benzene solution. On the other hand, the system Pb(OAc)$_4$–CF$_3$COOH–CH$_2$Cl$_2$ generated stable radicals whose structure is discussed below.

Results and Discussion

Applying the system Pb(OAc)$_4$–CF$_3$COOH–CH$_2$Cl$_2$ to the oxidation of 2,2-diacyl-1-arylhydrazines **1a–l**, stable radicals were detected by EPR spectroscopy. Their EPR spectra are (except for **1l**) characterized by the dominant splitting constants a_1(N) and a_2(N) from two nearly or fully equivalent nitrogen atoms. Although a_1(N) and a_2(N) values are in the range typical of hydrazyl radicals [5, 6], the oxidation of ^{15}N labelled compounds (**1b**, **1d**) provided experimental facts which are in contradiction with the above mentioned assignment. Considering the EPR parameters of all radicals observed, two different radical types are evaluated separately.

Radical Products from 1a–h

The radicals generated from **1a–h** were characterized by g-values ($g = 2.0031–2.0032$) somewhat lower than published data for hydrazyl radicals [5, 6]. The oxidation of the unlabelled compound **1a** afforded a radical whose EPR spectrum is represented by a 1:2:3:2:1 quintet. Using ^{15}N labelled hydrazine **1b** a 1:2:1 triplet EPR spectrum was recorded. A similar conclusion also follows from the analysis of the EPR spectra of radical products from **1c** and **1d**. The simulation of the high-resolved EPR spectrum recorded after the oxidation of **1d** (Fig. 1) clearly demonstrated the presence of two equivalent ^{15}N atoms ($a(^{15}\mathrm{N}) = 0.903$ mT). Simultaneously, two identical $a(^{14}\mathrm{N})$ splitting constants were found ($a(^{14}\mathrm{N}) = 0.095$ mT). Two pairs of equivalent nitrogen atoms were determined in the EPR spectra of radical products from **1e** and **1f**. In the case of the radical from **1g**, only splittings from two fully



1a–l

	X	Ar		X	Ar
a	1,2-C_6H_4	C_6H_5	**g**	1,2-C_6H_4	4-OCH_3-C_6H_4
b	1,2-C_6H_4	$C_6H_5(^{15}N_1)$	**h**	-CH_2-CH_2-	4-CH_3-C_6H_4
c	1,2-C_6H_4	4-CH_3-C_6H_4	**i**	1,2-C_6H_4	4-NO_2-C_6H_4
d	1,2-C_6H_4	4-CH_3-$C_6H_4(^{15}N_1)$	**j**	-CH_2-CH_2-	C_6H_5
e	1,2-C_6H_4	4-t-C_4H_9-C_6H_4	**k**	-CH_2-CH_2-CH_2-	C_6H_5
f	1,2-C_6H_4	4-Cl-C_6H_4	**l**	1,2-C_6H_4	2,4-(t-$C_4H_9)_2$-C_6H_3

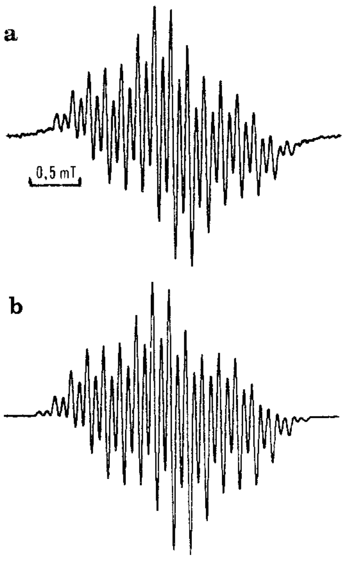
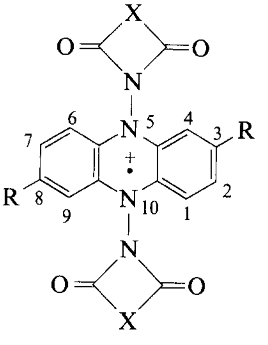


Fig. 1. Experimental (a) and simulated (b) EPR spectrum of phenazinium cation radical **5d**

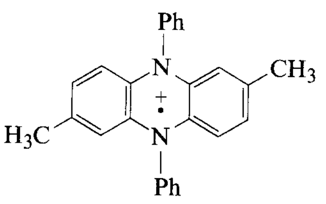
Table 1. EPR parameters of phenazinium cation radicals **5a–h**

Radical	Splitting constant (mT)				
	$a_N(5,10)$	$a_H(2,7)$	$a_H(3,8)$	$a_H(1,4,6,9)$	a_N(imid)
5a[a]	0.570	–	–	–	–
5b[a]	0.800[b]	–	–	–	–
5c	0.645	0.217	0.233	0.020	0.095
5d	0.903[b]	0.217	0.233	0.020	0.095
5e	0.645	0.220	–	–	0.100
5f	0.640	0.215	–	–	0.100
5g[a]	0.675	–	–	–	–
5h	0.645	0.217	0.233	–	0.095

[a] Splittings other than $a_N(5,10)$ unresolved; [b] splitting from ^{15}N labelled atoms



5a–h



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	X	R		X	R
a	1,2-C_6H_4	H	**e**	1,2-C_6H_4	t-C_4H_9
b	1,2-C_6H_5($^{15}N_{5,10}$)	H	**f**	1,2-C_6H_4	Cl
c	1,2-C_6H_4	CH_3	**g**	1,2-C_6H_4	CH_3O
d	1,2-C_6H_4($^{15}N_{5,10}$)	CH_3	**h**	-CH_2-CH_2-	CH_3

equivalent ^{14}N atoms were evidenced in the EPR spectrum. Due to the low resolution, no other splittings could be determined. Considering the EPR parameters, the radicals generated from **1a**–**h** are evidently the products of the dimerization reaction which are interpreted as phenazinium cation radicals **5a**–**h** (Table 1). This conclusion is supported by comparison of our EPR data with those relating to electrochemically generated phenazinium cation radicals [7–9]. For radical **6**, prepared by *Cauquis et al.* [8], the following EPR parameters are given: $g = 2.0028$, $a_N = 0.64$ mT (2N), $a_H = 0.21$ mT (6H), $a_H = 0.21$ mT (2H). Almost the same values were found for **5c** (additionally, the splitting constants $a_H = 0.02$ mT for protons in the positions 1, 4, 6, and 9 were observed in **5c** and **5d**). On the basis of experiments with ^{15}N labelled 2,2-diacyl-1-arylhydrazines **1b** and **1d**, we ascribe the splitting constants a_1(N) and a_2(N) to the N^5 and N^{10} atoms of the phenazine skeleton (described as N^1 in the starting 2,2-diacyl-1-arylhydrazine). The comparison of EPR data for radicals **5c** and **6** shows that the replacement of the phenyl substituent by the imidoyl ring does not significantly influence the spin density distribution within the phenazine system. No difference was found even when the imidoyl ring was altered (**5c** and **5h** exhibit identical EPR spectra). The existence of the cation radical **5c** was also confirmed by UV/Vis spectroscopy [10]. The parameters of UV/Vis spectra (**5c**: solvent: CF_3COOH/CH_2Cl_2. $\lambda_{max} = 390$ ($\varepsilon = 5900$), $\lambda_{Sh} = 504$ ($\varepsilon = 8000$), $\lambda_{max} = 540$ ($\varepsilon = 20000$). $\lambda_{Sh} = 650$ ($\varepsilon = 1000$), $\lambda_{max} = 680$ ($\varepsilon = 1100$), $\lambda_{Sh} = 720$ nm ($\varepsilon = 1000$)) were in good agreement with data reported for other phenazinium cation radicals. For example, 5-(3,7-dimethyl-10-p-tolyl-5,10-dihydro-5-phenazinioyl)-4-barbiturate [11] is characterized by the following parameters: solvent: $EtOH/H_2O$, $\lambda_{max} = 378$ ($\varepsilon = 6200$), $\lambda_{Sh} = 468$ ($\varepsilon = 6900$), $\lambda_{max} = 496$ ($\varepsilon = 13800$), $\lambda_{Sh} = 630$ ($\varepsilon = 1700$), $\lambda_{max} = 682$ ($\varepsilon = 2200$), $\lambda_{Sh} = 720$ nm ($\varepsilon = 2000$).

Apart from the phenazinium cation radicals **5a**–**h**, no other radicals were observed in the course of the oxidation of **1a**–**h** with the system $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2. According to *Cauquis et al.* [8], the formation of phenazinium cation radicals by the electrochemical oxidation of substituted diphenylamines proceeds through transient orthosemidines ($Ar_2N^\cdot$, $Ar_2\dot{N}H^+$, and Ar_2N^+ are assumed to be precursors), which undergo subsequent oxidative cyclization. However, the above mentioned reaction pathway was not confirmed by our experiments. No radicals were detected when the oxidation of orthosemidine from **1g** (prepared according to Ref. [1]) was carried out by the same procedure as with **1a–l**.

Radical Products from 1i–l

In the case of the radical products obtained by the oxidation of 2,2-diacyl-1-arylhydrazines **1i–l** ($g = 2.0035$), no complete identity of two basic nitrogen splittings $a_1(N)$ and $a_2(N)$ was proved in the EPR spectra. Therefore, we assign them to the corresponding hydrazyl radicals **2i–l**, and the $a_1(N)$ and $a_2(N)$ splittings are ascribed to the N^1 and N^2 atoms of the starting 2, 2-diacyl-1-arylhydrazines **1** (Table 2). No tendency towards the cyclization to the phenazinium cation radical **5** was observed (no changes in the EPR spectra were registered 15 minutes after the addition of the oxidation agent). Except for hydrazyl **2l**, only a limited resolution of the EPR spectra was achieved (Fig. 2). Besides $a(N^1)$ and $a(N^2)$ splitting constants, no other splittings were determined with **2i** and **2j**. Additional splitting constants of protons in *ortho* and *para* position of the phenyl ring were found in the EPR spectrum of **2k** (Fig. 2). The unusual spin density distribution in the case of **2l**, resulting in a relatively high ratio $a(N^1){:}a(N^2)$ and a high value of the splitting constant for the *ortho* proton ($a_H = 0.525$ mT), can be explained by a steric interaction due to the presence of a bulky *tert*-butyl group in the *ortho* position of the phenyl ring. The influence of the *ortho* substituents on the spin density distribution is well documented within the group of nitroxyl radicals (see *e.g. Yamauchi et al.* [12]). However, to date, similar studies concerning hydrazyl radicals are lacking [13].

To summarize, the oxidation of 2,2-diacyl-1-arylhydrazines **1a–l** with the system $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2 affords two types of radicals detectable by EPR spectroscopy (Scheme 2). In both cases, the basic splittings from two nitrogen atoms $a_1(N)$ and $a_2(N)$ were proved by the analysis of EPR spectra. The full equivalence of $a_1(N)$ and $a_2(N)$ characterizes phenazinium cation radicals **5a–h** generated by

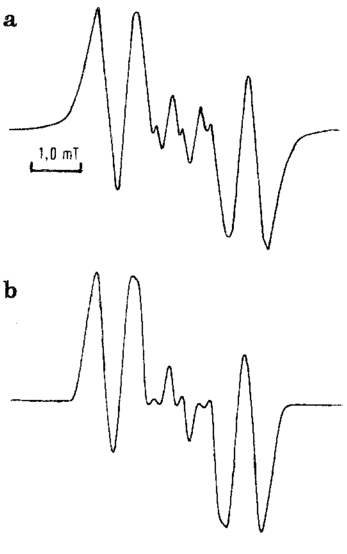
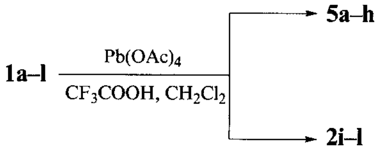


Fig. 2. Experimental (a) and simulated (b) EPR spectrum of hydrazyl radical **2k**



Scheme 2

Table 2. EPR parameters of hydrazyl radicals **2i–l**

Radical	Splitting constant (mT)				
	$a(N^1)$	$a(N^2)$		a_{other}	
2i	0.710	0.630		–	
2j	0.690	0.490		–	
2k	0.718	0.492	0.160 (2H);	0.170 (1H)	
2l[a]	0.945	0.141	0.525 (1H);	0.184 (1H);	0.142 (1H)

[a] Splitting constants taken from Ref. [3]

one electron oxidation of the corresponding phenazines. These are formed in a series of subsequent reactions where the primary products of the oxidation are taking part, one of them being probably hydrazyl radical **2**. In some cases, the consecutive rearrangement of hydrazyls **2** does not occur (**2i–l**) and these are observed as the final radical products of the oxidation.

Experimental

The synthesis of 2,2-diacyl-1-arylhydrazines **1a–l** has been described in previous papers [1, 2]. Their oxidation was carried out by the following procedure: In 2 ml of the system $Pb(OAc)_4$–CF_3COOH–CH_2Cl_2, prepared according to *Neugebauer* [4], 50 mg of the corresponding 2,2-diacyl-1-arylhydrazine were dissolved by stirring for 1 minute in a nitrogen atmosphere. For EPR measurements, 0.3 ml of the reaction mixture were used.

The EPR spectra were recorded with a Bruker EP 200E-SRC spectrometer, equipped with an Aspect 2000 computer. UV/Vis spectra were obtained with a Perkin Elmer Lambda 2 spectrometer.

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[10] The ε- values were calculated only from independent measurements of the radical concentration by EPR spectroscopy and titration with hydroquinone (20–25% radical yield). Attempts to isolate the corresponding intermediary phenazine were unsuccessful because the reaction mixture was composed of more than 10 products (HPLC) which could not be separated.

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[13] The hydrazoxyl radical **4l** ($g = 2.0057$) can be prepared by the oxidation of **1l** with t-BuO$_2^\cdot$ radicals generated by the decomposition of t-BuOOH with PbO$_2$. EPR parameters in mT ($a_N^{NO} = 1.302$, $a_N = 0.194$, $a_H^o = 0.160$, $a_H^m = 0.095$ (1H), $a_H^m = 0.058$ (1H)) document ortho effect of the tert-butyl group also in this case, especially when compared with EPR data of other hydrazoxyls **4** [2].

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