60. ESR Study of Nitroxide Radicals Generated from Triaz-2-en-1-ols

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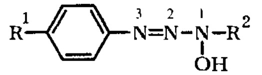
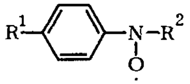
The triazenols 4-R^1–C_6H_4–N=N–N(OH)–R^2 (**1**), oxidized with *t*-$BuO_2^{\cdot}$ radicals, produced nitroxide radicals R^1–C_6H_4–N($O^{\cdot}$)–N=N(R^2)$^+O^-$ (**5**). The suggested radical structure was confirmed by ^{15}N-labeling. The reaction of triazenols **1** with PbO_2 proceeded under N_2 elimination, in which case nitroxides R^1–C_6H_4–N(R_2)–$O^{\cdot}$ (**2**) were observed as the final radical products. The intermediate R^1–$C_6H_4^{\cdot}$ radicals were identified by spin-trapping.

Introduction. – Although nitroxides represent one of the most intensively studied radical groups [1], only a few ESR data are reported on the radicals with the N–$O^{\cdot}$ function situated on a triazene skeleton. This fact can be explained by the marked tendency towards N_2 elimination accompanying the attempts to prepare them from triazenes as starting compounds. Earlier ESR studies have shown [2] [3] that the oxidation of triazenols 4–R^1–C_6H_4–N=N–N(OH)–R^2 (**1**; R^1 = H, NO_2; R^2 = *t*-Bu, Ph) with agents like alkaline $K_3[Fe(CN)_6]$ or PbO_2 leads to the nitroxides 4-R^1–C_6H_4–N(R^2)–$O^{\cdot}$ (**2**). Recently, a similar behavior was also confirmed for triazenes 4-R^1–C_6H_4–N=N–NH–R^2, in which case radicals **2** were observed on oxidation with 4-nitrobenzenecarboperoxoic acid, and alkoxy aryl nitroxides 4-R^1–C_6H_4–N($O^{\cdot}$)–O(*t*-Bu) were detected by the oxidation with *t*-$BuO_2^{\cdot}$ radicals [4]. As more efficient method for the preparation of triazenoxy radicals, the spin-trapping reaction of nitroso compounds with photolytically generated N-radicals was found [5] [6].



1a R^1 = H, R^2 = Me
b R^1 = Bu, R^2 = Me
c R^1 = CN, R^2 = Me
d R^1 = MeO, R^2 = Me
e R^1 = Bu, R^2 = C_6H_{11}
f R^1 = Bu, R^2 = C_6H_{11} (^{15}N-labeling of N(2))
g R^1 = H, R^2 = C_6H_{11} (^{15}N-labeling of N(3))



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Within the framework of this paper, we have aimed at a generation of triazenoxy radicals from a series of triaz-2-en-1-ols **1** with the system *t*-BuOOH/PbO_2, effectively operating as a source of *t*-BuO$_2^{\cdot}$ radicals [7]. In comparison with other works, the experimental conditions were appropriately modified with the aim to prevent N_2 elimination during oxidation. To establish the role of the hydroperoxide decomposer itself, the reaction of triazenols **1** with PbO_2 was separately investigated, the radical intermediates having been identified by spin trapping.

Experimental. – *Syntheses.* Methyl-substituted ($R^2 = Me$) and cyclohexyl-substituted ($R^2 = C_6H_{11}$) triaz-2-en-1-ols **1a–g** ((*E*)-isomers) were synthesized according to the procedure described in [8].

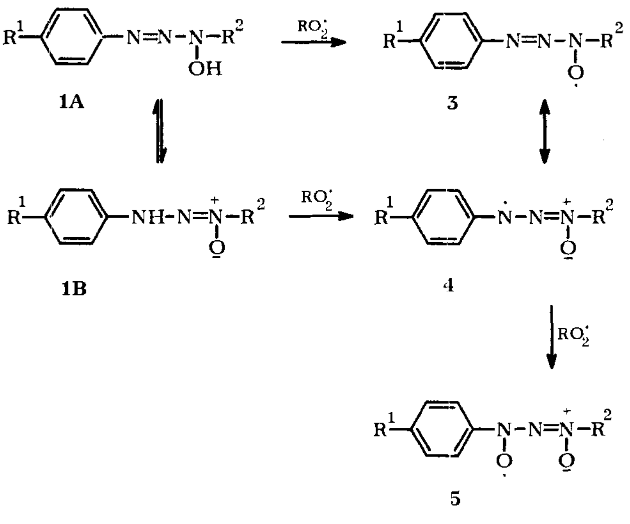
Oxidation of **1** *with* t-*BuOOH/PbO*$_2$. At r.t., **1** was dissolved in a 10^{-2} M benzene soln. of *t*-BuOOH (molar ratio **1**/*t*-BuOOH 1:1). For the generation of *t*-BuO$_2^{\cdot}$, PbO_2 (10 mg) was suspended in 2 ml of this soln. and stirred for 2 min. After sedimentation of the heterogeneous phase, 0.5 ml of the soln. were transferred into the ESR cell. Before the ESR measurements, Ar was bubbled through the mixture for a short time.

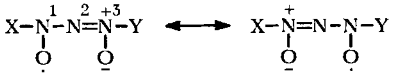
Oxidation of **1** *with PbO*$_2$. Performing the oxidation under the same conditions as above, no radicals were detected in the absence of *t*-BuOOH. The addition of a greater amount of PbO_2 (50 mg) produced radical products which were assigned to nitroxide radicals **2**. In spin-trapping experiments, nitrosodurene (= 1,2,4,5-tetramethyl-3-nitrosobenzene; ND) was added to the starting system (molar ratio triazene/ND 1:1).

ESR Spectra: *Bruker-200D* spectrometer equipped with an *Aspect 2000* computer.

Results and Discussion. – From the structural point of view, triazenols **1**, which are assumed to occur in tautomeric forms **1A** and **1B** [2] [9] (see *Scheme 1*), appear to be suitable starting compounds for the preparation of triazenoxy radicals. In our experiments, *t*-BuO$_2^{\cdot}$ radicals, generated by the reaction of *t*-BuOOH and PbO_2, were employed as the attacking agent. To avoid the simultaneous decomposition of **1** by PbO_2, the latter was added in a small portion to the benzene solution of *t*-BuOOH and triazenol **1**. In this way, high-resolution ESR spectra were obtained whose *g*-value ($g \approx 2.0054$) suggested the generation of nitroxide radicals. The large number of interacting nuclei, however, excluded their assignment to the nitroxide radicals **2**. Owing to the possible existence of tautomeric forms **1A** and **1B**, the reaction pathways leading to nitroxide radicals **3** and **5** had to be taken into account (*Scheme 1*).

Scheme 1





$$\mathrm{X{-}\underset{\underset{\cdot}{O}}{\overset{1}{N}}{-}\overset{2}{N}{=}\underset{\underset{-}{O}}{\overset{+3}{N}}{-}Y} \longleftrightarrow \mathrm{X{-}\underset{\underset{-}{O}}{\overset{+}{N}}{=}N{-}\underset{\underset{\cdot}{O}}{N}{-}Y}$$

6A **6B**

According to *Rehorek* and *Marx* [5], the nitroxide radicals of type **3** were present in the mixture of several radical adducts formed by the photolysis of some diazonium salts in the presence of nitroso spin traps (ArN$_2^\cdot$ + RNO → ArN$_2$–N(O$^\cdot$)-R) in CH$_2$Cl$_2$. From the multicomponent ESR spectrum, the a_N splitting constants of three nonequivalent N-atoms (a_N = 1.01, 0.32, and 0.13 mT) were determined for nitroxide **3**. On the other hand, nitroxide radicals X–N(O$^\cdot$)–N=N(Y)$^+$O$^-$ (**6**) which are similar to the suggested structure **5** were supposed to be generated by the spin trapping of N$_3^\cdot$ radicals with either nitrosodurene or the binary spin-trap system *t*-BuNO/nitrosodurene [6]. In addition to the a_N(N(2)) = 0.238 mT, the splitting constants from two equivalent N-atoms (a_N(N(1))=a_N(N(3)) = 0.721 mT) were found due to the symmetrical substitution (X = Y = durene ring). These results can be interpreted by mesomerism. In the presence of asymmetrical substitution (X = durene ring, Y = *t*-Bu), three different a_N splitting constants (a_N(N(1)) = 0.870, a_N(N(3)) = 0.660, and a_N(N(2)) = 0.220 mT) were evidenced.

Reflecting these facts, we focused our attention on the detailed characterization of nitroxide radicals generated from triazenols **1** by means of *t*-BuO$_2^\cdot$ radicals. A representative experimental and simulated ESR spectrum of the nitroxide radical obtained from **1a** is

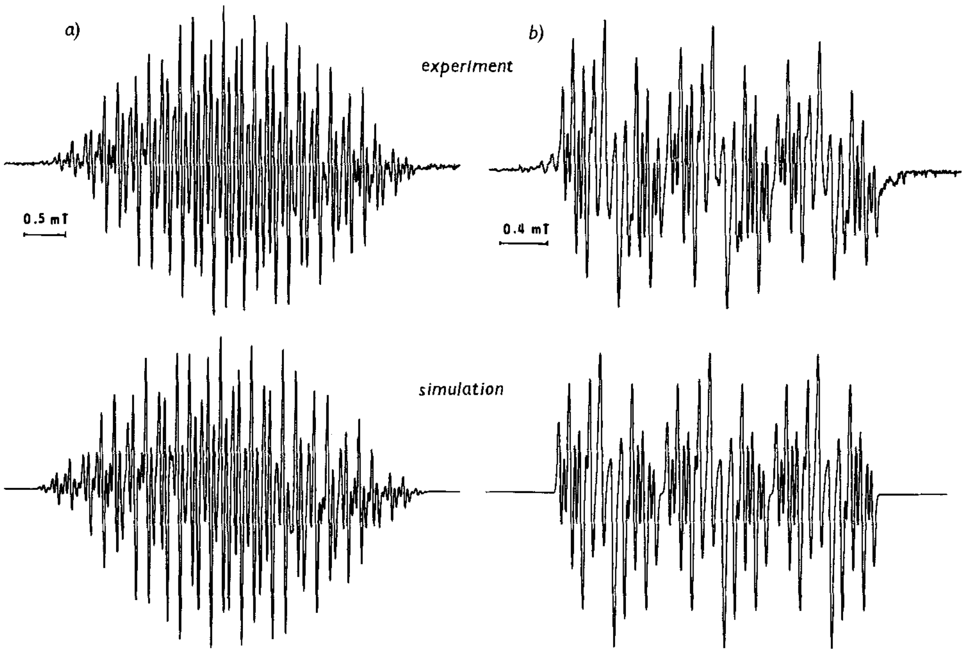


Fig. a) *Experimental and simulated ESR spectrum of nitroxide radical generated by the oxidation of* **1a** *with* t-*BuO$_2^\cdot$ radicals* (the spectrum is assigned to structure **5a**); b) *experimental and simulated ESR spectrum of radical adduct* **7c** shown in the *Figure, a*. The splitting constants of *ortho-* and *meta*-protons with average values 0.170 and 0.062 mT, respectively, as well as those of protons in substituents R^1 and R^2 ($a_H(R^1)$ and $a_H(R^2)$), were found for all nitroxides prepared from **1a–g**. Similarly, the a_N splitting constants of three N-atoms with average values 0.834, 0.572, and 0.162 mT were evidenced in all ESR spectra. These facts suggested that under given experimental conditions, the reaction of **1a–g** with t-BuO$_2^{\cdot}$ radicals apparently proceeded in accordance with *Scheme 1*, *i.e.*, without elimination of N_2. Because, in this case, the structures **3** and **5** (theoretically exhibiting an equal number of interacting nuclei) have to be considered, the unambiguous assignment can be achieved by ^{15}N-labeling. This approach was applied using triazenols **1f** (^{15}N-labeling at N(2)) and **1g** (^{15}N-labeling at N(3))[1]). In the nitroxide radical generated from **1f**, replacement of ^{14}N by ^{15}N enhanced the corresponding splitting constant a_N(N(2)) from 0.173 to 0.225 mT. On the other hand, in the nitroxide radical generated from **1g**, a splitting constant for the ^{15}N-labelled atom N(3) of 1.250 mT was determined, corresponding to $a_N(N(3)) = 0.892$ mT of the unlabeled radical. The comparison with the a_N values of the nitroxide radical prepared from unlabelled compound **1e** unambiguously confirmed that the isotopic replacement occurred on the N-atom bearing the major part of the spin density. The sequence of a_N splitting constants $a_N(N(3)) > a_N(N(1)) > a_N(N(2))$ showed that nitroxide radicals **5** are generated by the oxidation of **1a–g** with t-BuO$_2^{\cdot}$ radicals, whereas the alternative structure **3** is excluded.

5A[1])   **5B**

With respect to the mesomerism expressed by the two principal contributing structures **5A** and **5B**, the R^2-substitution in **1a–g** (R^2 = Me, cyclohexyl) greatly increases the contribution of the mesomeric form **5A**. In accordance with this effect, the asymmetric distribution of the spin density on atoms N(1) and N(3) resulting in the different values $a_N(N(1))$ and $a_N(N(3))$ was observed. The a_H(Me) values in nitroxide radicals prepared from **1a–d** were also indicative of structure **5**. It is known that in methyl aryl nitroxides Ar–N(O$^{\cdot}$)–Me (Ar = substituted phenyl), these values are comparable with a_N(NO) splitting constants [10], whereas in our case they represent *ca.* 50% of a_N(NO) values (*Table 1*). This fact can be explained on the basis of the preferential contribution of the mesomeric form **5A**. Consequently, the Me group in nitroxide **5** does not exhibit the typical ESR parameters of the alkyl group attached to the radical centre, as would be expected in nitroxide radical **3**.

Although the above-mentioned experimental data are in favor of structure **5** rather than of **3**, comparative quantum-chemical calculations were also performed. To determine the unpaired spin-density distribution in radicals **3a** and **5a**, the AM1 method was utilized [11], as implemented in the AMPAC package [12]. The effect of spin contamination was eliminated by the projection of UHF wavefunctions using the spin-projection method. In the case of **3a**, the N-splitting constants $a_N^{calc}(N(3)) = 0.459$,

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[1]) For convenience, the radicals produced from the triazenols **1** are numbered in the same way.

Table 1. *Splitting Constants of Nitroxide Radicals* **5a–g** *Prepared by the Reaction of* t-*BuO*$_2^{\cdot}$ *Radicals with Triazenols* **1a–g** *in Benzene*

Radical	R^1	R^2	Splitting constants/mT1)						
			a_N(NO)	a_N(N(2))	a_N(N(1))	$a_H(R^2)$	a_H^o	a_H^m	$a_H(R^1)$
5a	H	Me	0.825	0.165	0.570	0.418	0.171	0.057	0.171
b	Bu	Me	0.820	0.181	0.585	0.433	0.165	0.058	0.124
c	CN	Me	0.810	0.124	0.510	0.338	0.193	0.069	0.026a)
d	MeO	Me	0.823	0.180	0.617	0.470	0.160	0.060	0.027
e	Bu	C_6H_{11}	0.867	0.173	0.576	0.173b)	0.162	0.062	0.125
f	Bu	C_6H_{11}	0.860	0.225c)	0.580	0.177b)	0.170	0.062	0.123
g	H	C_6H_{11}	1.250c)	0.150	0.570	0.130b)	0.175	0.064	0.175

a) Splitting constant of the N-atom. b) Splitting constant of 1 H of the cyclohexyl group. c) Splitting constant of the ^{15}N-labeled atom.

a_N^{calc}(N(2)) = 0.253, and a_N^{calc}(N(1)) = 0.853 mT were obtained, *i.e.*, the highest a_N splitting constant was ascribed to the N-atom of the >N–O$^{\cdot}$ group. In contrast to **3a**, the sequence of calculated a_N splitting constants in **5a** (a_N^{calc}(N(3)) = 0.796, a_N^{calc}(N(2)) = 0.312, and a_N^{calc}(N(1)) = 0.467 mT) was in good agreement with that experimentally observed.

The oxidation of triazenes **1** with t-BuO$_2^{\cdot}$ radicals is an extraordinarily efficient method for the selective preparation of triazenoxy radicals **5**. These were still detectable in benzene solution 1 h following their generation at room temperature. In CH_2Cl_2, their stability was substantially lower, and only rapidly decaying ESR signals of radicals **5** were observed. Increasing the temperature to 70°, the low concentration of alkyl aryl nitroxide R^1–C_6H_4–N(O$^{\cdot}$)–R^2 (**2**) was detected as a result of N_2 elimination. Subsequently, the experiments were also carried out with other oxidative agents such as dibenzoyl peroxide (DBPO) or 4-nitrobenzenecarboperoxoic acid (4-NBPA). The heating of triazenols **1** and DBPO (10^{-2} M benzene solution of both substances) did not lead to any radical products at 40 and 50°. At 60°, only a weak unresolved ESR signal appeared which could not be interpreted. The treatment with 4-NBPA unambiguously afforded nitroxide **5**. Although their occurrence is beyond any doubt, the ESR spectrum was more complex, owing to the simultaneous existence of further radicals in the reaction mixture.

Decomposition of Triazenols **1a–g** *with PbO*$_2$. As mentioned above, besides the reaction of t-BuO$_2^{\cdot}$ radicals, a simultaneous decomposition of triazenols **1** initiated by PbO_2 occurred. In standard experiments, its contribution was negligible owing to the small amount of PbO_2 in the system t-BuOOH/PbO_2/**1**. Because no radicals were observed upon oxidation of **1** in the absence of t-BuOOH with the equivalent amount of PbO_2, this assumption appears to be acceptable. Performing the experiment with a substantially higher quantity of PbO_2 (50 mg PbO_2, *i.e.*, 5 times more in comparison with the standard experiment), the ESR spectra of alkyl aryl nitroxides **2** were obtained (*Table 2*). Their formation is in accordance with earlier observations reported by *Razuvaev et al.* [3]. The reaction mechanism presumes a formation of radical **3** and **4** from **1A** and **1B** in the first step of the oxidation reaction and their subsequent decomposition under N_2 elimination, as outlined in *Scheme 2*. The same experiment carried out in the presence of nitrosodurene led to the formation of diaryl nitroxide radicals 4-R^1-C_6H_4–N(O$^{\cdot}$)-Dur (**7**), the only radical adducts observed (*Scheme 2*). Their ESR parameters are summarized in *Table 3*. The high-resolution ESR spectra of the nitroxides **7** gave evidence of the partial

Table 2. *Splitting Constants of Nitroxide Radicals* **2a–g** *Prepared by the Reaction of* PbO_2 *with Triazenols* **1a–g** *in Benzene*

Radical	R^1	R^2	Splitting constants/mT				
			a_N (NO)	a_H (R^2)	a_H^o	a_H^m	a_H (R^1)
2a	H	Me	1.048	0.973	0.280	0.093	0.280
b	Bu	Me	1.055	0.980	0.280	0.095	0.215
c	CN	Me	0.942	0.887	0.263	0.090	0.037[a]
d	MeO	Me	1.105	1.007	0.280	0.092	0.032
e[b][c]	Bu	C_6H_{11}	1.085	–	–	–	–
g[c]	H	C_6H_{11}	1.085	–	–	–	–

[a] Splitting constant of the N-atom. [b] Identical splitting constants were obtained from **1f**. [c] Splittings other than a_N (NO) unresolved.

Scheme 2

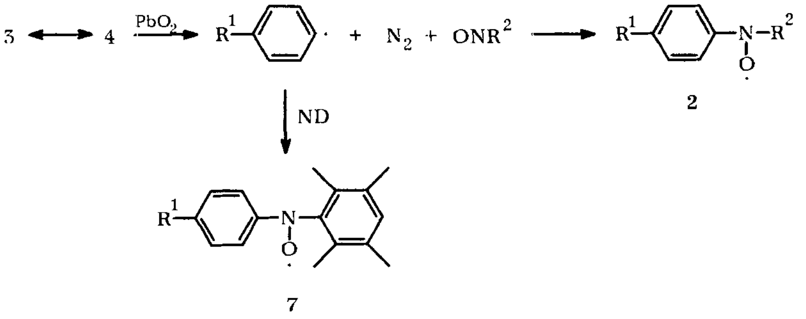

Table 3. *Splitting Constants of Radical Adducts* **7a–d** *Prepared by the Reaction of* PbO_2 *with Triazenols* **1a–g** *in the Presence of Nitrosodurene*

Radical	R^1	Splitting constants/mT			
		a_N(NO)	a_H^o	a_H^m	a_H(R^1)
7a[a]	H	1.016	0.270 0.290	0.090 0.096	0.280
b[b]	Bu	1.032	0.270 0.286	0.087 0.095	0.217
c	CN	0.942	0.265 0.284	0.094 0.099	0.039[c]
d	MeO	1.090	0.262 0.292	0.080 0.090	0.037

[a] Identical splitting constants were obtained from **1a** and **1g**. [b] Identical splitting constants were obtained from **1b**, **1e**, and **1f**. [c] Splitting constant from the N-atom.

nonequivalence of two *ortho*-protons (and also two *meta*-protons) of the *para*-substituted benzene ring. This phenomenon, resulting from the steric influence of the durene ring, was not described in the case of spin adducts of 4-R-aryl radicals with nitrosodurene [13] (protons in *ortho*- or *meta*-positions are considered to be equivalent), although the steric effects in *ortho*-methylated diaryl nitroxids were experimentally and theoretically studied many years ago [14]. This fact can be attributed either to low resolution of ESR spectra or to the imperfect simulation. The effect of nonequivalence was more evident in radicals **7c** (*Fig. b*) and **7d** where the splitting constants of R^1 were low (a_N(CN) = 0.039 mT in **7c** and a_H(MeO) = 0.037 mT in **7d**). In adducts **7a** and **7b**, a small deviation from the equivalence resulted only in a small change of the ESR line intensities and can possibly be disregarded.

Conclusions. – Owing to the presence of the >N–OH fragment in triazenols **1a–g**, these compounds are expected to be suitable starting compounds for the preparation of corresponding nitroxide radicals. However, as documented by ESR experiments, the reaction pathway is influenced by several factors which cannot be ignored. On the one hand, an occurrence of two tautomeric forms, **1A** and **1B**, has to be considered, on the other, a tendency towards N_2 elimination is generally a characteristic feature of triazenes during their oxidation [2–4], resulting in the generation of secondary nitroxide radicals. The experimental conditions were described enabling the generation of primary nitroxide radicals from triazenols **1a–g** for the first time. Their oxidation with *t*-$BuO_2^{\cdot}$ radicals (prepared by the decomposition of *t*-BuOOH with PbO_2) afforded nitroxide radicals **5a–g** whose structure was confirmed by ^{15}N-labeling. To prevent the decomposition of **1a–g** with PbO_2, the oxidation was carried out at an optimum molar ratio of *t*-BuOOH, PbO_2, and triazenol **1**. Separately, the reaction of PbO_2 with compounds **1a–g** leading to secondary nitroxide radicals **2a–g** was investigated where the intermediate aryl radicals were evidenced using the nitrosodurene spin-trap.

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