# FREE RADICAL REACTIONS OF N-HYDROXYTRIAZENES

# THAT CONTAIN BULKY SUBSTITUENTS

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Previously we had shown [1-3] that 1-aryl-3-tert-alkyl-3-hydroxytriazenes undergo free radical decomposition under the influence of oxidizing agents in solution. The simultaneous formation of aryl radicals and nitroso compounds during the decomposition makes it possible to use the N-hydroxytriazenes when studying the various reactions of Ar' in solution by the EPR spectroscopy method. Here the selection of R is dictated both by the relative simplicity of interpreting the EPR spectra and the stability of the formed nitrogen oxides, as well as the stability of the nitroso compounds. tert-Butyl derivatives (tert-nitrosobutane, phenyl-tert-butylnitrone) are used most frequently when fixing the radicals. The Ar' that are liberated in the decomposition of the 1-aryl-3-tert-butyl-3-hydroxytriazenes are fixed by tert-nitrosobutane with the formation of quite stable aryl-tert-butylnitrogen oxides (Scheme 1). However, the starting product for the synthesis of the tert-butyl alcohol and ur a [4] proceeds in low yield. It seemed interesting to synthesize some N-hydroxytriazenes, containing R in the 3 position, that would be more readily available than the tert-butyl analog. For this purpose we synthesize and studied the oxidative decomposition of hydroxytriazenes with the following structure.

 $\begin{array}{ccc} Ph-N=N-N-C(CH_{2}OCR)_{8} \\ & | & | \\ OH & O \\ R=CH_{8} & (I); & C_{6}H_{5} & (II); & CH_{2}C_{6}H_{5} & (III) \end{array}$ 

The insertion of bulky tertiary groups into the triazene made it possible to observe the steric effects that are associated with a change in the geometry of the radical center and with the ease of intramolecular rotation around the C-NO bond in the nitroxide radicals. Trimethylolnitromethane served as the starting compound for the synthesis, which is easily obtained from  $CH_3NO_2$  and  $(CH_2O)_n$  [5].

 $\begin{array}{c} CH_{3}NO_{2} + 3CH_{2}O \xrightarrow{KOH} (HOCH_{2})_{3}C - NO_{2} \\ (HOCH_{2})_{3}C - NO_{2} + 3(RCO)_{2}O \rightarrow \left(R - C \begin{pmatrix} O \\ OCH_{2} \end{pmatrix}_{3}C - NO_{2} + 3RCOOH \\ \left(R - C \begin{pmatrix} O \\ OCH_{2} \end{pmatrix}_{3}C - NO_{2} \xrightarrow{A1/Hg} \left(R - C \begin{pmatrix} O \\ OCH_{2} \end{pmatrix}_{3}CNHOH \\ \left(R - C \begin{pmatrix} O \\ OCH_{2} \end{pmatrix}_{3}CNHOH + PhN_{2}CI \rightarrow Ph - N = N - N - C(CH_{2}OCR)_{3} \\ OH & O \end{array}\right)$ 

Hydroxytriazenes (I)-(III) are colorless crystalline compounds that are stable under ordinary conditions and are moderately soluble in organic solvents. The oxidation of (I)-(III) with  $PbO_2$  in  $C_6H_6$  leads to decomposition according to Scheme 1. The EPR signal of the nitroxides Ph-N-R is observed in the

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# solution during reaction.

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TABLE 1. Hyperfine Coupling (HFC) Constants of S-N-R Radicals

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Com- pound	s	R	a <sub>N</sub>	a <sup>o</sup> H	$a_{\mathrm{H}}^{p}$	$a_{\mathrm{H}}^{m}$	$a_{ m H}^{m eta}$
(1a)	Ph	C(CH <sub>a</sub> ) <sub>3</sub>	12.30	1.80	1_80	0.80	_
(IIa)	Ph	C(CH₂OCCH₃)₃ ∥ O	12,70	1,65	1,33	1,33	-
(IIIa)	Ph	C(CH₂OCPh)₃ ∥ O	12,70	1,59	1,25	1,25	-
(IVa)	Ph	C(CH2OCCH2Ph)3	12,70	1,24	1,24	1,24	
(V)	CH3	C(CH <sub>3</sub> ) <sub>3</sub>	15,80		_		11,70
(VI)	CH3	C(CH2OCCH3)3	14,70			_	12,20
(VII)	CH3	C(CH₂OCCH₂Ph)₃ Ŭ	14,80	-	-	_	12,10
(VIII)	PhCHCH₃	C(CH <sub>3</sub> ) <sub>3</sub>	14,80	-	-	`	3,50
(IX)	PhCHCH <sub>3</sub>	C(CH <sub>2</sub> OCCH <sub>3</sub> ) <sub>3</sub>	13,70		-	-	3,20
(X)	PhCHCH3	C(CH2OCCH2Ph)3 O	13,70	-	-	_	3,60
(XI)	PhCH₂	C(CH <sub>3</sub> ) <sub>3</sub>	15,00	_	_	-	7,50
(XII)	PhCH <sub>2</sub>	C(CH₂OCCH₃)₃ ∥ O	13,70	-		-	7,80
(XIII)	PhCH <sub>2</sub>	C(CH <sub>2</sub> OCCH <sub>2</sub> Ph) <sub>3</sub>	13,70	-		-	8,00

\* Solvents: C<sub>6</sub>H<sub>6</sub> (Ia) -(IVa), CH<sub>3</sub>I(V) -(VII), and a 3 : 1 toluene-ethylbenzene mixture (VIII) -(XIII).

where  $R = C(CH_3)_3$ ,  $C(CH_3)_2ON = C(CH_3)_2$ , SH - solventScheme 1

The spectra of radicals (IIa)-(IVa) are characterized by a different ratio of the splitting constants on the protons of the ring when compared with nitroxide (Ia) (Table 1), which is apparently associated with the presence of bulky substituents on the nitrogen atom of nitroxides (IIa)-(IVa). In the given case a change in the character of the distribution of the spin density in the ring can be attributed to a disturbance of the coupling of the unpaired electron with the  $\pi$ -electron system of the ring, caused by a turning of the plane of the ring with respect to the radical center N-O due to steric hindrance.

The use of hydrocarbons and halo derivatives as solvents in the oxidation of (I)-(III) makes it possible to record the EPR spectra of the nitroxides S-N-R (see Scheme 1). The parameters of the spectra for  $\dot{S}$ 

=  $CH_3$ ,  $PhCH_2$ , and  $PhCHCH_3$ , containing various R, are given in Table 1. In the case of nitroxides (VI)-(VII), (IX)-(X), and (XII)-(XIII) a decrease is observed in the nitrogen constant when compared, respectively, with (V), (VIII), and (XI), which is apparently associated with the peculiarities in the geometric

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TABLE 2. HFC Constants of Nitroxides R-N-R' and  $(R)_2N-O'$ 

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Compound	R'	R	a <sub>N</sub>
(XIV)	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	15,40
(XV)	H5C2C(CH3)2	C(CH <sub>s</sub> ) <sub>3</sub>	15,20
(XVI)	H5C2C(CH3)2	C(CH₂OCCH₂Ph)₃ ∥ O	14,20
(XVII)	$H_{\delta}C_{2}C(CH_{3})_{2}$	C(CH <sub>2</sub> OCCH <sub>3</sub> ) <sub>3</sub>	14,20
(XVIII)	C(CH2OCCH3)3	C(CH2OCCH3)3 II O	13,60
(XIX)	C(CH2OCPh)3	C(CH₂OCPh)3 ∥ O	13,50
(XX)	C(CH <sub>2</sub> OCCH <sub>2</sub> Ph) <sub>3</sub>	C(CH <sub>2</sub> OCCH <sub>2</sub> Ph) <sub>3</sub> U	13,30
(XXI)	$H_5C_2C(CH_3)_2$	C(CH <sub>2</sub> OCPh) <sub>3</sub>	13,00
(XXII)	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH2OCPh)3	13,10



structure of the radical center. A number of authors [6-8] speak in support of the pyramidal structure of the  $\sum N-O$  fragment for aliphatic nitroxides. This viewpoint is corroborated by the data of the x-ray structure analysis of some nitroxides [9] and the results of the quantum mechanical calculations [6, 7]. When going from the planar

structure of the nitroxide group to the pyramidal structure the proportion of the N-O' increases when compared with the ionic structure  $N-O^-$ . Here the density of the unpaired electron increases by  $2p_Z$ - AO O and decreases by  $2p_Z$ -AON, which should be accompanied by a decrease in the nitrogen constant. At the same time, the transition from sp<sup>2</sup> to sp<sup>3</sup> hybridization of the nitrogen atom when the geometry of the paramagnetic center changes is responsible for the appearance of the contribution of the s-component to the unpaired electron orbital, which leads to a noticeable increase in the constant of the isotropic HFC on the nitrogen atom. Calculations show [6, 7] that an increase in the angle of deviation  $\alpha$  of the  $\sigma$ -bonds of the N atom from the  $\sigma$ -plane of CNC in nitroxides is accompanied by an increase in  $a_N$ .

Taking the above said into consideration and assigning the structure with a nonplanar structure of the radical center to nitroxides (V)-(XIII), it may be assumed that in all cases an increase in the bulk of the substituents will be accompanied by repulsion effects, which lead to a decrease in the angle of deviation of the bonds of the N atom from the  $\sigma$ -plane (Fig. 1). Here the s/p ratio in the unpaired electron orbital decreases, which is the reason for the decrease in the nitrogen constant in nitroxides of structure S  $-N-C(CH_2OCR)_3$  when compared with the tert-butyl analogs.

The dependence of the  $\beta$ -proton constant on the size of the substituents attached to the nitrogen atom of nitroxides is expressed to a lesser degree. Some decrease in  $a_{\rm H}^{\beta}$  in radical (V) when compared with (VI) and (VII) is found to be in agreement with the data given in [6] for the case of the free rotation of the CH<sub>3</sub> group. The most favorable conformation for nitroxides (XI)-(XII) will apparently be conformation A, with an angle of  $\theta \approx 60^{\circ}$  [10]. Starting with the simple MacConnel equation  $a_{\rm H}^{\beta} = B \cos^2 \theta$ , the value of the  $\beta$ -proton splitting can be estimated approximately, which for the case  $\theta = 60^{\circ}$  is found to be in the range 7-8 Oe, which is in agreement with our experimental data. The difference in the  $a_{\rm H}^{\beta}$  constants for (XI)-(XIII) is slight, which indicates the close values of the barrier for different R. The value of  $a_{\rm H}^{\beta}$  for (VIII)-(X) is close to the value 3.2 Oe, which was obtained in [10] for the  $\beta$ -proton constant in the radical-anion  $\frac{CH_3}{C_2H_5}$  CH- $\dot{NO}_2$ . The preferred conformation in this case will be conformation B with  $\theta = 90^{\circ}$ .

The dependence of the value of the nitrogen constant on the size of the tert-alkyl groups was also observed in the EPR spectra of a number of nitroxide radicals of structure R-N-R' and  $(R)_2N-O'$  (Table

2). The bis-alkyl nitroxides were obtained by the irradiation of the corresponding tert-nitroso compounds in benzene solution.

$$RN = 0 \xrightarrow{hv} (R)_2 N = 0$$

Nitroxide radicals (XV)-(XVII) and (XXI)-(XXII) are observed during the oxidative cleavage of 1phenyl-3-R-3-hydroxytriazenes in benzene in the presence of neopentyl bromide  $C_6H_6$  and tert-butyl bromide (XXII). A decrease in  $a_N$  when going from (XIV) to (XXII)



gives reason to assume that the same order holds for the increase in the repulsion of R and the decrease in the angle  $\alpha$ .

#### EXPERIMENTAL METHOD

The EPR spectra were recorded on a RE-1301 radiosepctrometer.

The 2-nitro-2-methylol-1,3-propanediol and trimethylolnitromethane acetate were synthesized as described in [5].

<u>1-Phenyl-3-tris(acetoxymethylene)methyl-3-hydroxytriazene (I)</u>. 1) To a solution of 5 g (0.02 mole) of trimethylolnitromethane acetate in 150 ml of ether was added 8 g of aluminum amalgam. Then 5 ml of water was added in drops at such a rate that the ether boiled vigorously all the time. After 20 min the ether solution, containing the trimethylol-N-methylhydroxylamine acetate, was decanted from the Al(OH)<sub>3</sub> precipitate and the ether was removed under vacuum. The hydroxylamine was obtained as colorless crystals, mp 70-71°.

2) To a stirred solution of 5.2 g (0.02 mole) of trimethylol-N-methylhydroxylamine acetate in aqueous alcohol (1:1), cooled to 5-7°, was added a solution of phenyldiazonium chloride, which had been prepared from 1.9 g (0.02 mole) of aniline, 1.35 g of sodium nitrite, 5.3 ml of HCl and 5.3 ml of H<sub>2</sub>O, and neutralized with sodium acetate to pH 7. After 1 h the obtained crystalline precipitate was filtered and recrystallized from aqueous alcohol; yield 35%, mp 109°. Found: C 52.32; H 6.00; N 11.60%.  $C_{16}H_{21}N_3O_7$ . Calculated: C 52.31; H 5.77; N 11.43%.

<u>1-Phenyl-3-tris(benzoxymethylene)methyl-3-hydroxytriazene (II).</u> 1) A mixture of 27.60 g (0.12 mole) of benzoic anhydride [11] and 5 g (0.03 mole) of trimethylolnitromethane was heated until solution was obtained, and then refluxed for 30 min. A thick mass was obtained on cooling, which was washed with NaHCO<sub>3</sub> solution to remove the benzoic acid. Recrystallization from acetone gave colorless crystals of trimethylolnitromethane tribenzoate. The compound was reduced to the hydroxylamine the same as indicated for (I). Recrystallization from alcohol gave trimethylol-N-methylhydroxylamine tribenzoate as colorless crystals with mp 95-96°.

2) The hydroxylamine was coupled with phenyldiazonium chloride in the same manner as described for (I). The isolated dark yellow oil gradually crystallized; yield 30%; mp 129-130° (from alcohol). Found: C 67.57; H 5.01; N 7.35%.  $C_{31}H_{27}N_3O_7$ . Calculated: C 67.25; H 4.93; N 7.59%.

<u>1-Phenyl-3-tris(phenylacetoxymethylene)methyl-3-hydroxytriazene (III).</u> 1) A mixture of 6 g (0.04 mole) of phenylacetic acid and 2.8 g (0.02 mole) of  $PCl_3$  was heated on the steam bath for 1 h. The acid chloride was decanted from the  $H_3PO_4$ , 2.2 g (0.02 mole) of trimethylolnitromethane was added, and the mixture was heated on the steam bath for 1 h. The tris(phenylacetoxymethylene)nitromethane, which was obtained as a light yellow oil, was washed with water and dissolved in 150 ml of ether. Reduction to the hydroxylamine was run the same as in the case of (I) and (II). Tris(phenylacetoxymethylene)-N-methyl-hydroxylamine was obtained as colorless crystals with mp 80-82° (from alcohol).

2) The coupling of 6.5 g (0.013 mole) of the hydroxylamine with an acetic acid solution of phenyldiazonium chloride (1.23 g of aniline, 0.89 g of sodium nitrite, 3.5 ml of HCl and 3.5 ml of H<sub>2</sub>O) was run the same as in the case of (I) and (II). The obtained light yellow oil was separated, which gradually crystallized. Colorless crystals of (III) were obtained in 45% yield after a double recrystallization from a 2:1 alcohol-pentane mixture, mp 63-64°. Found: C 68.51; H 5.57; N 7.29%.  $C_{34}H_{33}N_3O_7$ . Calculated: C 68.52; H 5.58; N 7.05%.

Trimethylolnitrosomethane acetate was obtained as described in [5]. The same method was used to obtain trimethylolnitrosomethane benzoate (mp 142-143°) and tris(phenylacetoxymethylene)nitrosomethane (mp 56-57°). The nitroso compounds are colorless crystalline substances that are moderately soluble in alcohol and ether, and more readily soluble in benzene, with the formation of blue solutions.

### CONCLUSIONS

1. A number of N-hydroxytriazenes, containing bulky tertiary aliphatic groups in the 3-position, was synthesized and their oxidative decomposition was studied.

2. A study was made of the decomposition of the synthesized hydroxytriazenes in some organic solvents and the obtained EPR spectra were discussed. The structure of the tertiary alkyl groups affects the character of the HFC and the value of the splitting constant.

3. A number of tertiary nitroso compounds was synthesized. The EPR spectra of nitroxides with the structure R-N-R' and  $(R)_2N-O'$  were obtained.

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