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Chemistry of α-Nitro Sulfones. V.[1] An Electron Spin Resonance Spectroscopic Study of Arylsulfonylalkyl Alkoxy Nitroxides, the Spin Adducts of Arylsulfonylalkanenitronic Acid Esters

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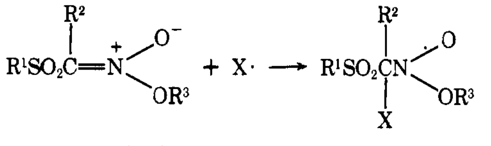
Abstract: Arylsulfonylalkanenitronic acid esters were obtained upon reaction of five α-nitro sulfones with diazomethane or diazoethane. Four of these products readily add a variety of radicals to produce arylsulfonylalkyl alkoxy nitroxides which were studied by ESR spectroscopy. If the trapped radical is bulky, two nitrogen hyperfine splitting constants are observed. We infer that these nitroxides occur in two favored conformations, both with the α-carbon to sulfonyl bond eclipsed with the half-filled orbital on nitrogen. The same types of nitroxides could also be generated by reaction of α-nitro sulfones with alkoxycarbinyl radicals. When the α-nitro sulfone contains a chiral center and the groups attached to the carbinyl radical site are different from each other, diastereomeric nitroxides are formed. The dependence of the nitrogen hyperfine splitting constant on the substitution pattern in the nitroxides is discussed. The reaction of several nitronic acid esters with lead tetraacetate led to the production of α-sulfonyl iminoxy radicals. This reaction most likely proceeds via thermal decomposition into α-oximino sulfones and subsequent oxidation.

The spin trapping technique[2,3] has proven to be extremely useful for the detection and identification in solution of paramagnetic species which are too short-lived to be studied directly by electron spin resonance (ESR) spectroscopy under the employed reaction conditions. Of the various spin traps, monomeric *C*-nitroso compounds and nitrones occupy a paramount position. Both types of compounds often scavenge rapidly and efficiently short-lived radicals to afford relatively stable nitroxide radicals that are conveniently studied by means of ESR. The relative merits of these and other spin trapping agents[4-8] as well as the applicability and pitfalls of the method have been discussed extensively.[2,3] Besides its usefulness in mechanistic and analytic investigations, the spin trapping technique has also a considerable potential for the production of radicals of intrinsic interest otherwise difficult to prepare.

We anticipated that possibilities of this kind could be explored when we prepared five arylsulfonylalkanenitronic acid esters in the course of our continuing investigations on α-nitro sulfones.[1] Should these species behave like nitrones, then addition of free radicals, X·, would lead to the previously unreported arylsulfonylalkyl alkoxy nitroxides[9] (eq 1). This expectation was borne out in practice and, moreover, the generated nitroxides turned out to be versatile probes for the study of subtle conformational and electronic perturbations[10] induced by varying R^2 and R^3. Variation of R^3 was accomplished more easily by using a different method for the production of the nitroxides, i.e., the direct addition of free radicals to α-nitro sulfones.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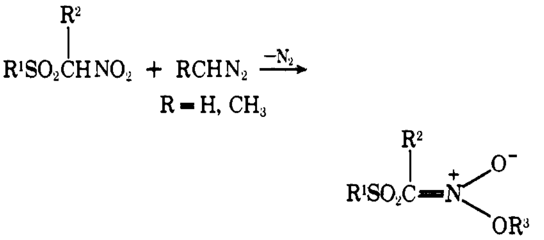
Results and Discussion

Arylsulfonylalkanenitronic Acid Esters. The nitronic acid esters **1–5** were prepared by alkylation of the appropriate α-nitro sulfones with diazomethane or diazoethane (eq 2).


(2)

1, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = H$; $R^3 = CH_3$
2, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = R^3 = CH_3$
3, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = C_6H_5$; $R^3 = CH_3$
4, $R^1 = C_6H_5$; $R^2 = H$; $R^3 = CH_3$
5, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = H$; $R^3 = C_2H_5$

Previously, Arndt and Rose[11] have described **1** as a pungent, viscous, yellow oil which resisted crystallization. In our hands **1–3** crystallized readily and could be obtained analytically pure. The crude **4** and **5** were not purified further, but were used immediately in the ESR experiments. Although **1–5** in principle can exist as geometrical isomers, the above synthetic procedure afforded only one isomer for **1–3** and **5** as indicated by NMR analysis. Isomerization of **1** was observed during recrystallization leading to a 1:1

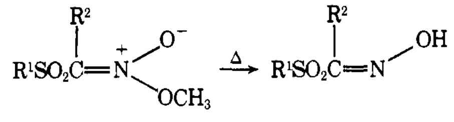
Table I. Hyperfine Splitting Constants[a] of Arylsulfonylalkyl Alkoxy Nitroxides. The Use of Nitronic Acid Esters **1, 2,** 4, and 5 as Spin Traps (Equation 1)

Nitroxide	Spin trap	Trapped radical	T (°C)	A_N	A_{H_β} (1 H)	A_{H_γ}[b]	A_{H_γ}
6	**1**	$C_6H_5\dot{C}H_2$	−60	25.6	1.8 (4 H)		0.3 (2 H)
				~25.3	1.8 (4 H)		0.3 (2 H)
7	1	$C_6H_5\dot{C}HCH_3$	−20	25.7	0.6	1.8 (3 H)	*c*
				24.6	~0.6	~1.8 (3 H)	
8	**1**	C_4H_7O[d]	−60	26.4	0.9	1.9 (3 H)	*c*
				25.5	0.9	1.9 (3 H)	
9	1	$CH_3\dot{C}HOC_2H_5$	−60	25.7	1.0	2.0 (3 H)	*c*
				25.3	1.0	2.0 (3 H)	
10	1	$(CH_3)_2\dot{C}OCH(CH_3)_2$	−20	26.0	0.5	2.0 (3 H)	
				24.2	~0.5	~2.0 (3 H)	
11	**1**	$\dot{C}H_2OH$	−20	25.5	1.5 (4 H)		0.3 (2 H)
12	**1**	$CH_3\dot{C}HOH$	−20	25.5	1.0	1.9 (3 H)	*c*
				25.1	1.0	1.9 (3 H)	
13	1	p-$CH_3C_6H_4SO_2\cdot$	−20	24.4	0.6	1.6 (3 H)	
				23.9	0.5	1.9 (3 H)	
14	1	$(CH_3)_3CO\cdot$[e]	−60	25.6	1.0	1.8 (3 H)	
				~25.3	1.0	1.8 (3 H)	
15	**2**	C_4H_7O[d]	−60	26.1[f]		1.8 (3 H)	*c*
16	**2**	$CH_3\dot{C}HOC_2H_5$	−60	25.5		1.8 (3 H)	0.4 (3 H)
				24.5		1.8 (3 H)	0.4 (3 H)
17	**2**	p-$CH_3C_6H_4SO_2\cdot$	−60	23.8[f]		1.8 (3 H)	*c*
18	4	$C_6H_5\dot{C}H_2$	−60	25.6	1.8 (4 H)		0.3 (3 H)
				~25.3	1.8 (4 H)		0.3 (3 H)
19	4	$(CH_3)_3CO\cdot$[e]	−60	25.6	1.0	1.8 (3 H)	
				~25.3	1.0	1.8 (3 H)	
20	5	$C_6H_5\dot{C}H_2$	−60	25.0	1.5 (3 H)		*c*
				~24.8	1.5 (3 H)		
21	5	$CH_3\dot{C}HOC_2H_5$	−60	25.5	1.0	1.9 (2 H)	*c*
				24.9	1.0	1.9 (2 H)	

[a] Hfsc's in gauss. Solvent: CH_2Cl_2. In those cases where two sets of hfsc's are given, these data refer to the isomeric species discussed in the text. [b] $A_{H\gamma}$ of alkoxy group. [c] Not resolved. [d] 2-Tetrahydrofuryl radical. [e] See text. [f] Second A_N not detectable because of the low quality of the spectrum as a result of low thermal stability.

mixture of the *E* and *Z* isomers. Apparently, attack of the diazoalkane on **1–3** and **5** usually occurs preferentially at one of the nitro oxygen atoms.

Thermal decomposition of **2** and **3** in boiling dichloromethane gave the corresponding oximes in yields of 43 and 38%, respectively.[12] This reaction constitutes a useful and facile alternative procedure for the preparation of α-oximino sulfones. Synthesis of these compounds in the past involved treatment of α-nitro sulfones with sodium nitrite.[13] Arndt and Rose[11] have reported the formation of p-tolylthiocarbimide upon heating of **1** at 95°. However, we were unable to detect this product, either with GLC or with ir techniques. Upon decomposition of **1** at lower temperature (41°), 3,4-bis(p-tolylsulfonyl)furoxan (4.4%) was the only compound we could isolate.



$$R^1SO_2\overset{\overset{\displaystyle R^2}{|}}{C}=\overset{+}{N}\begin{smallmatrix}O^-\\ OCH_3\end{smallmatrix} \xrightarrow{\Delta} R^1SO_2\overset{\overset{\displaystyle R^2}{|}}{C}=N-OH$$

2, 3

Arylsulfonylalkyl Alkoxy Nitroxides Derived From 1, 2, 4, and 5. Table I lists the hyperfine splitting constants (hfsc's) of the arylsulfonylalkyl alkoxy nitroxides **6–21** obtained upon addition of various types of radicals to the nitronic acid ester function of **1, 2, 4,** and **5** (eq 1). The radicals X· were prepared in situ by photolysis of di-*tert*-butyl peroxide (DTPO) in the presence of the appropriate compounds bearing abstractable hydrogen atoms. Blank experiments showed that no ESR signals were detectable when the photolyses were carried out in the absence of DTPO. Although p-tolylsulfonyl radicals could be generated by hydrogen abstraction from the parent sulfinic acid, these radicals are best produced by photolysis of p-tolylsulfonyl iodide.[14] Both methods gave ultimately ESR spectra of the same spin adducts. The stability of the spin adducts derived from **1, 4,** and **5** is rather low which necessitates ESR measurements at well below room temperature. After interruption of the uv irradiation, the ESR signal disappeared within a minute. The instability of the nitroxides derived from **2** is even greater and we were unable to obtain ESR evidence for spin trapping by **3**. The latter observation is suggestive for the importance of steric factors for addition and/or decay.

The structural assignment of **6–21** is mainly based on the characteristic high A_N values,[15] the internal consistency of A_N and A_H values within the series, and the possibility of generating these types of nitroxides by an independent method, i.e., addition of free radicals to α-nitro sulfones (vide infra). Furthermore, the hfsc's and multiplicities of the proton signals of the alkoxy moiety are very similar to those reported by Forshult et al.[9a] for alkyl alkoxy nitroxides. In some cases, resolution of hyperfine splittings due to coupling with γ-hydrogen atoms introduced by the trapped radicals was possible (Table I). Among the series of newly prepared nitroxides, only the identity of **14** and **19** is not certain. These species were produced in the absence of additives possessing readily abstractable hydrogen atoms. Since the hfsc's of **14** and **19** are identical, hydrogen abstraction

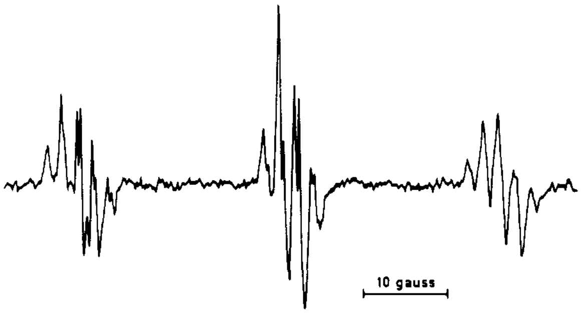


Figure 1. ESR spectrum of 7.

from the tolyl methyl group of **1** can be excluded. Attack at the methoxy group of **1** and **4** should also be considered in view of the same order of reactivity of anisole and toluene toward hydrogen abstraction by *tert*-butoxyl radicals.[16] The derived nitroxide is then expected to exhibit a β-H hyperfine splitting constant of ca. 1.7 G as is found for **6**, **11**, **18**, and **20**. Since the observed A_{H_β} is significantly lower, we tentatively propose that **14** and **19** are produced via trapping of *tert*-butoxyl radicals. Support for this view is found in the observation that *tert*-butoxyl radicals are trapped by phenyl *tert*-butyl nitrone.[17] More detailed inspection of the ESR spectra of **6–21** reveals that in many cases line-broadening of the high-field and low-field nitrogen lines occurs together with pattern changes of these lines (Figure 1).

Selective line-broadening of the nitrogen $M_{\mathrm{N}} = \pm 1$ lines has been previously noted by Sleight and Sutcliffe[18] for some aryl alkoxy nitroxides. For a possible explanation, these authors referred to reports[19] in which similar effects have been rationalized in terms of the anisotropy of nitrogen hyperfine couplings and g tensors. Recently, however, hindered rotation around the C–N bond has been detected[20] for several alkoxy nitroxides derived from nitro-substituted heterocyclic aromatic compounds. Hence, we infer that hindered rotation is an alternative explanation for the observations of Sleight and Sutcliffe.[18] In our case, the pattern change of the $M_{\mathrm{N}} = \pm 1$ lines is not reconcilable with anisotropic line-broadening and is clearly indicative for the presence of two closely related paramagnetic species which possess (a) only slightly different A_{N} values in the region characteristic for alkyl alkoxy nitroxides and (b) virtually the same g values and hydrogen hfsc's in view of the complete overlap of the $M_{\mathrm{N}} = 0$ lines (Figure 1).[21] These data lend strong support to the hypothesis that we are dealing with magnetically inequivalent conformations which interconvert at a rate comparable with, or slower than, the nitrogen hyperfine frequency difference found for the individual rotamers.

In order to exclude an alternative possibility, namely the presence of two diastereomeric nitroxides originating from a slow flip at the bent nitrogen center adjacent to an asymmetric carbon atom, the ESR spectrum of **13** was carefully recorded at −20° using a small modulation amplitude (Figure 2). Clearly two different species are present at this temperature, thereby ruling out this possibility, since the carbon atom attached to nitrogen is not chiral in this nitroxide. By proper adjustment of the line width and by chosing the right hfsc's we were able to simulate the spectrum (Figure 3).

To gain more insight into the conformational isomerism, it is worthwhile to consider the A_{N} values more closely (Table I). The high A_{N} values usually observed[9] for alkyl alkoxy nitroxides have been explained in terms of significant s character of the half-filled orbital. From the anisotropy of the nitrogen splitting a 2p:2s ratio of 11.6 has been calculated for the orbital containing the unpaired electron.[22] For the closely related[5] nitroalkane anion radicals this ratio is 11.4. These results are indicative for nonplanarity of the respective radical centers. In fact, for such high oxygenated radical centers bending away from planarity is expected[22-24] in view of similar effects found for, for instance, the 1,3-dioxolan-2-yl radical.[24] Comparison of the A_{N} values given in Table I with those of simple alkyl alkoxy nitroxides (A_{N} = 27–30 G)[9] shows that the nitrogen hfsc's of **6–21** are reduced by ca. 3–4 G. That this is not exclusively due to the inductive effect of the sulfonyl group is demonstrated by the A_{N} value of **13** which is not significantly reduced further by the presence of an additional sulfonyl moiety. We suggest that steric effects are also effective, because a bent configuration (around nitrogen) for the species $\mathrm{R^1N(OR^2)O\cdot}$ with bulky groups $\mathrm{R^1}$ and $\mathrm{R^2}$ will suffer significantly more steric compression than a more planar one.[22] Thus, the radical center will adopt a less bent configuration with increasing steric bulk of the groups $\mathrm{R^1}$ and $\mathrm{R^2}$, resulting in a decrease of the s character of the orbital containing the unpaired electron and in a concomitant lower A_{N} value. Therefore, we propose that a large difference between the A_{N} values of the rotamers of **6–21** may reflect a large difference in steric compression in both species.[25] This idea receives support from the observation that the spin adduct of a highly branched radical like **10** has ΔA_{N} = 1.8 G, whereas for **6** ΔA_{N} = 0.3 G. However, the situation is still more complicated. Following arguments of Gilbert and Trenwith[22] to explain the reduced A_{N} value observed for $\mathrm{{}^-O_3SCH_2NO_2\cdot^-}$, we suggest that the $\mathrm{C_\alpha{-}SO_2}$ bond in ar-

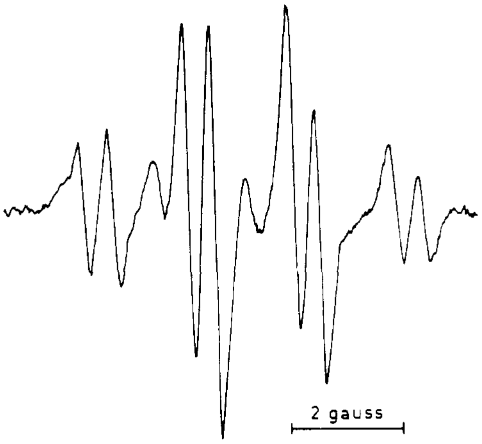


Figure 2. Low-field nitrogen line of **13**.

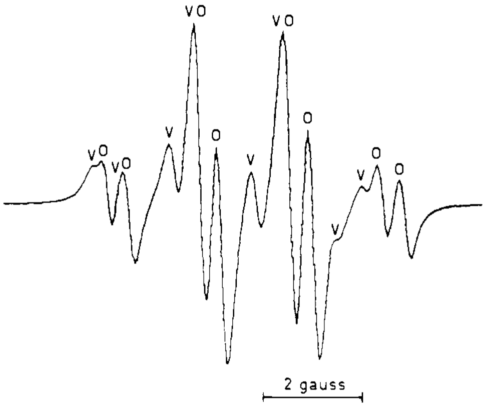
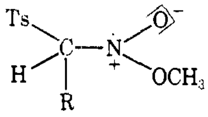
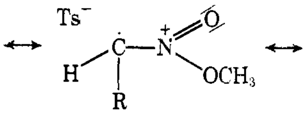


Figure 3. Computer simulated low-field nitrogen line of **13**. Rotamer ratio is 3:1.

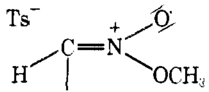
ylsulfonylalkyl alkoxy nitroxides will have a definite tendency to eclipse the orbital containing the free spin in order to maximize interactions of the type represented by the resonance hybrids **22b** and **22c** (cf. $\cdot CH(OH)CH_2OH$[24]).[26]



22a

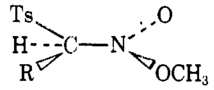


22b

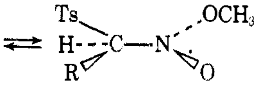


22c

The contribution of **22b** and **22c** will be associated with stretching of the C_α-SO_2 bond and flattening[27] of the nitrogen center in the radical and, consequently, with a reduction of A_N. Support for the C_α-SO_2 bond stretching is found in the rapid elimination of sulfinate anion[28] from the structurally related α-nitro sulfone anion radicals, $R^1SO_2CR^2R^3NO_2\cdot^-$. It should be emphasized that one may not calculate the dihedral angle between the planes defined by the axis of the half-filled orbital on nitrogen, the N-C_α and the C_α-H_β bonds by means of the simple Heller-McConnell relation,[29] because this equation does not hold for nonplanar radical centers. However, the generally low A_{H_β} values of the nitroxides listed in Table I certainly indicate that in both rotamers the C_α-H_β bond lies close to the plane perpendicular to the axis of the π-like orbital on nitrogen. The rotamers should then be assigned structures in which the C_α-H_β bond is in approximately trans or cis position with respect to the $N\dot{-}O$ group (cf. **23a**-**23b**). In addition to



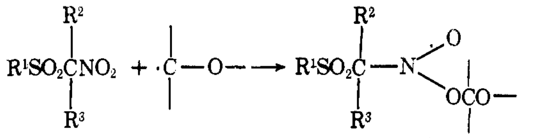
23a



23b

the C_α-SO_2 bond eclipsing effect, the barrier to internal rotation around the C-N bond may be enhanced as a result of the pyramidal configuration at the nitrogen radical site. Unfortunately, the thermal instability of **6**-**21** precludes ESR investigation at temperatures sufficiently high for line-shape analysis of the exchange process.[30]

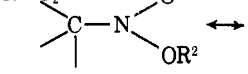
Arylsulfonylalkyl Alkoxy Nitroxides Derived from α-Nitro Sulfones. In an attempt to generate alkoxy nitroxides similar to those described in the previous section by a different method, i.e., the addition of simple alkyl radicals to α-nitro sulfones, no spin adducts were observed. This agrees well with the previous report that methyl radicals are not scavenged by nitro compounds.[5] By contrast, alkoxycarbinyl radicals readily add to α-nitro sulfones to give arylsulfonylalkyl alkoxy nitroxides (eq 3). The reaction may proceed via initial electron transfer,[5,31] but this will imply that the combination of the ions thus formed is more rapid than decomposition of the α-nitro sulfone anion radical.[1b,28]



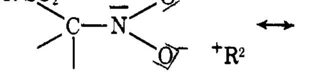
$$R^1SO_2C(R^2)(R^3)NO_2 + \cdot\overset{|}{\underset{|}{C}}-O- \longrightarrow R^1SO_2C(R^2)(R^3)-N(\dot{O})-O\overset{|}{\underset{|}{C}}O- \quad (3)$$

24-25

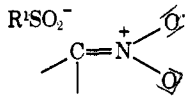
The alkoxycarbinyl radicals were prepared in situ via α-hydrogen abstraction from ethers by *tert*-butoxyl radicals. The thermal stabilities of the adducts **24**-**45** are usually higher than those of **6**-**21**. ESR parameters are shown in Table II. Several interesting features emerge from these data. First of all, we note the magnetic inequivalency of the methylene protons in **26**, **27**, and **29**. Similar observations have been reported previously by Sleight and Sutcliffe[9b] and they attributed this phenomenon to steric interactions between the alkyl and alkoxy groups. This explanation, however, cannot be reconciled with the equivalency of the methylene protons in **28**. Therefore we assume that we are dealing with *diastereotopic* protons, since the inequivalency was *temperature independent* (+20 to − 60°) and only observed when the trapped alkoxycarbinyl radical generates an asymmetric center in the nitroxide. A slow exchange process was only detected for **28**, which showed line-broadening of the central line of the triplets at low temperatures (−60 to −90°). This line-width alternation is indicative for a slow conversion (on the ESR time scale) between two favored conformations apparently not involving rotation around the C_α-N bond (see previous section). Second, the elatively low A_N values of a number of alkoxy nitroxides listed in Table II are noteworthy. As argued before, an increasing steric bulk imposed by the alkoxy group encumbering the radical center will decrease A_N. This effect is modulated by the conformational preferences discussed in the previous section.[32] In view of the reduction of A_N found for **25** as compared with **27**, we infer that the electron donating ability of the alkoxycarbinyl radical is also effective in determining A_N. We propose that some heterolytic stretching of the C_β-O_α bond can occur in **24**-**45**, which will induce anion radical character in the alkoxy nitroxide structure (**46a**-**46b**). This effect will be accompanied by a decrease in A_N,[5] which will be most pronounced for the most stable cationic R^2 group. The very small A_{H_γ} (not resolved) for the alkoxy methylene group of **30**, as compared with A_{H_γ} = 1.5 G for **20**, is also consistent with a stretching of the C_β-O_α bond. In view of the well-known leaving ability of sulfinate groups from α-nitro sulfone anion radicals,[28,33] the hybrid structure **46c** will further contribute to a flattening of the nitrogen center (vide supra).



46a



46b



46c

Different A_N values are not expected for the nitroxides **24**-**29** and **40**-**45**, because both preferred conformations of these radicals (see previous section) are identical. Only one A_N value was also observed in the case of **30**, **31**, and **34**. This can be tentatively rationalized by assuming that C_β-O_α bond stretching has occurred to such an extent that the difference in strain between both rotamers has been largely eliminated.

It is interesting to note that upon reaction of an α-nitro sulfone *containing a chiral center* with a carbinyl radical *with three different groups attached to the radical site*, two alkoxy nitroxides with different A_N values are observed. Figure 4 typically illustrates these types of spectra. We associate this observation with the presence of two *diastereomeric* nitroxides.[34]

Many of the nitroxides recorded in Table II, including radicals with an achiral C_α atom, exhibit selective line-broadening depending on M_N and to lesser extend on M_H. Especially for **37** the high-field nitrogen line was smaller than the low-field nitrogen line, which in turn was smaller

Table II. Hyperfine Splitting Constants[a] of Arylsulfonylalkyl Alkoxy Nitroxides Obtained from α-Nitro Sulfones (Equation 3)

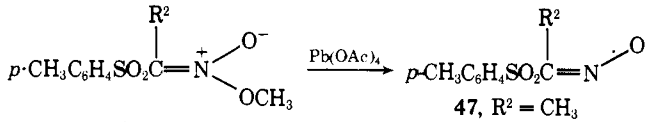
	α-Nitro sulfone							
Nitroxide	R^1	R^2	R^3	Trapped radical	T (°C)	A_N	A_{H_β}	A_{H_γ}
24	p-$CH_3C_6H_4$	H	H	$C_6H_5O\dot{C}H_2$	+23	26.5	4.9 (2 H)	*b*
25	p-$CH_3C_6H_4$	H	H	$C_3H_5O_2$[c]	+30	23.6	5.2 (2 H)	*b*
					−90	23.5	4.6 (2 H)	
26	p-$CH_3C_6H_4$	H	H	$CH_3\dot{C}HOC_2H_5$	+10	25.2	5.5 (1 H)	*b*
							4.9 (1 H)	
27	p-$CH_3C_6H_4$	H	H	C_4H_7O[d]	+20	24.4	5.8 (1 H)	*b*
							4.7 (1 H)	
28	p-$CH_3C_6H_4$	H	H	$(CH_3)_2\dot{C}OCH(CH_3)_2$	−20	22.8	4.1 (2 H)	
29	p-$CH_3C_6H_4$	H	H	$C_6H_{11}O$[e]	−20	22.2	4.3 (1 H)	
							3.7 (1 H)	
30	p-$CH_3C_6H_4$	CH_3	H	$C_6H_5O\dot{C}H_2$	−20	26.8	2.2 (1 H)	*b*
31	p-$CH_3C_6H_4$	CH_3	H	$C_3H_5O_2$[c]	−20	23.8	3.1 (1 H)	0.4 (3 H)
32	p-$CH_3C_6H_4$	CH_3	H	$CH_3\dot{C}HOC_2H_5$	−60	27.4	2.0 (1 H)	*b*
						25.7	2.0 (1 H)	
33	p-$CH_3C_6H_4$	CH_3	H	C_4H_7O[d]	+20	24.7	4.3 (1 H)	*b*
						24.0	2.6 (1 H)	
34	p-$CH_3C_6H_4$	CH_3	H	$(CH_3)_2\dot{C}OCH(CH_3)_2$	−60	22.9	1.8 (1 H)	0.4 (3 H)
35	p-$CH_3C_6H_4$	CH_3	H	$C_6H_{11}O$[e]	−20	23.7	1.8 (1 H)	
						21.2	2.3 (1 H)	
36	p-$CH_3C_6H_4$	C_2H_5	H	C_4H_7O[d]	+20	24.6	2.7 (1 H)	*b*
						23.1	2.2 (1 H)	
37	p-$CH_3C_6H_4$	C_2H_5	H	$C_3H_5O_2$[c]	−40	23.0	2.1 (1 H)	0.5 (1 H)
38	p-$CH_3C_6H_4$	C_2H_5	H	$(CH_3)_2\dot{C}OCH(CH_3)_2$	−60	22.6	1.6 (1 H)	~0.3 (2 H)
39	p-$CH_3C_6H_4$	C_2H_5	D	C_4H_7O[d]	−60	24.5		*b*
						23.0		
40	p-$CH_3C_6H_4$	CH_3	CH_3	$C_6H_5O\dot{C}H_2$	−20	25.2		*b*
41	p-$CH_3C_6H_4$	CH_3	CH_3	$C_3H_5O_2$[c]	−60	23.4		0.2 (6 H)
42	p-$CH_3C_6H_4$	CH_3	CH_3	C_4H_7O[d]	−60	23.5		0.2 (6 H)
43	p-$CH_3C_6H_4$	CH_3	CH_3	$(CH_3)_2\dot{C}OCH(CH_3)_2$	−60	23.3		0.2 (6 H)
44	p-$CH_3C_6H_4$	$(-CH_2-)_5$		C_4H_7O[d]	−60	23.5		*b*
45	p-$CH_3C_6H_4$	$(-CH_2-)_5$		$C_6H_{11}O$[e]	−60	23.0		*b*

[a] Hfsc's in gauss. Solvent: CH_2Cl_2 except for **24**, **27**, **30–34**, **36**, **39**, **40**, and **44** where the ether was used as the medium. In those cases where two sets of hfsc's are given, these data refer to the isomeric species discussed in the text. [b] Not resolved. [c] 1,3-Dioxolan-2-yl radical. [d] 2-Tetrahydrofuryl radical. [e] 2,5-Dimethyltetrahydrofuran-2-yl radical.

than the central nitrogen line. These changes might be attributed to anisotropic line-broadening.

In addition to the alkoxy nitroxides, we observed often the formation of other types of nitroxide radicals with A_N values of ca. 11 G. This was especially the case when the more crowded arylsulfonylalkyl alkoxy nitroxides were generated at relatively high temperatures. We are probably dealing here with decay products,[35] which could be produced by trapping of alkoxycarbinyl radicals with generated α-nitroso sulfones.

Iminoxy Radicals from 1-3. When solutions of **2** or **3** in dichloromethane were treated with lead tetraacetate at room temperature, radicals were generated which gave ESR spectra identical with those of the α-sulfonyl iminoxy radicals **47** and **48**. Recently these types of iminoxy radicals have been described.[36]



$$p\text{-}CH_3C_6H_4SO_2\overset{R^2}{\overset{|}{C}}{=}\overset{+}{N}(O^-)OCH_3 \xrightarrow{Pb(OAc)_4} p\text{-}CH_3C_6H_4SO_2\overset{R^2}{\overset{|}{C}}{=}N\dot{O}$$

2, $R^2 = CH_3$
3, $R^2 = C_6H_5$

47, $R^2 = CH_3$
48, $R^2 = C_6H_5$

These species presumably originate via thermal decomposition of **2** and **3** into the corresponding oximes followed by oxidation. Treatment of **1** under similar conditions led to the formation of three relatively stable paramagnetic species. Their ESR spectra were characterized by the following hfsc's: (i) A_N = 30.2 G, A_H = 7.2 (1 H) G; (ii) A_N = 30.5 G; and (iii) A_N = 9.6 G, A_H = 1.6 (1 H) G. The first spectrum is identified as that of the corresponding *syn*-sulfonyl iminoxy radical by (a) comparison of the A_N value with those of *syn*-sulfonyl iminoxy radicals[36] (29.0-30.3 G) and (b) by comparison of the A_H value with that of the cor-

Figure 4. ESR spectrum of **32**.

responding *syn*-benzoyl iminoxy radical (6.5 g).[37] The origin of the spectra (ii) and (iii) is as yet uncertain.

Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. A. F. Hamminga. Melting points were determined using a Mettler FP2 melting point apparatus with a Mettler FP21 microscope attachment. NMR spectra were recorded on a Varian A-60 spectrometer, using TMS ($\delta = 0$) as an internal standard. Ir spectra were measured with a Perkin-Elmer instrument, Model 257. The ESR spectra were recorded on a Varian E-4 apparatus fitted with a Varian A-1268 variable temperature controller. The accuracy of A_N and A_H is dependent on the stability of the nitroxide; for **6–12, 14–21, 32, 33, 35, 36,** and **39** $\Delta A_N = \pm 0.3$ G and $\Delta A_H = \pm 0.2$ G; for the other nitroxides, $\Delta A_N = \pm 0.2$ G and $\Delta A_H = \pm 0.1$ G. The ESR spectra of the nitroxides **13, 33,** and **35** have been satisfactorily simulated by using the hfsc's recorded in Tables I and II.

The α-nitro sulfones were prepared according to our previously described method[1b] or according to the method of Truce et al.[38] The other chemicals were commercial products and were adequately purified before use. The solutions used for the ESR experiments contained 20% (v/v) of di-*tert*-butyl peroxide, 20% (v/v) of the appropriate compound bearing abstractable hydrogen atoms, 60% (v/v) of dichloromethane, and about 0.1–0.2 g of α-nitro sulfone or nitronic acid ester/milliliter of solvent. All solutions were purged with nitrogen for 20 min prior to photolysis, in order to remove dissolved oxygen. Photolyses were carried out by irradiation of the samples directly in the cavity by means of a Philips SP 500-W lamp.

General Procedure for the Preparation of the Nitronic Acid Esters 1–5. Solutions of the appropriate α-nitro sulfones (20 mmol) in 25–50 ml of CH_2Cl_2 were treated with an excess of diazomethane. The solutions were stirred for 1 hr at 0–5°, whereafter the solvent was removed in vacuo. Upon dilution of the colorless viscous oils with some ether and standing for 15 hr at −20° in a refrigerator, the nitronic acid esters **1–3** crystallized. Filtration and subsequent recrystallization gave the pure compounds. The nitronic acid ethyl ester **5** was obtained by reaction of the parent compound with diazoethane. This compound, as well as **4**, was not further purified but used directly in the ESR experiments.

Nitronic Acid Methyl Ester from *p*-Tolylsulfonylnitromethane (1). Yield 57%; mp 65.7–67.2° dec (from ether–*n*-hexane); NMR ($CDCl_3$) δ 2.45 (s, 3 H, aryl CH_3), 3.70 (s, 3 H, OCH_3), 7.33 (s, 1 H, vinyl proton), 7.3–8.1 ppm (m, 4 H, aryl protons); ir (KBr) 3100, 1600, 1330, 1150 cm^{-1}.

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.16; H, 4.83; N, 6.11; S, 13.99. Found: C, 47.12; H, 4.81; N, 6.07; S, 13.84.

Recrystallization from EtOAc–*n*-hexane caused isomerization (*E*:*Z* ratio of 1:1). Mp 55.4–71.6° dec; NMR ($CDCl_3$), additional absorptions δ 3.77 (s, 3 H, OCH_3), 6.98 (s, 1 H, vinyl proton), 7.3–8.1 ppm (m, 4 H, aryl protons).

Nitronic Acid Methyl Ester from 1-Nitro-1-(*p*-tolylsulfonyl)ethane (2). Yield 52%; mp 65.0–65.3° dec (from EtOAc–*n*-hexane); NMR ($CDCl_3$) δ 2.45 (s, 6 H, vinyl CH_3 and aryl CH_3), 3.73 (s, 3 H, OCH_3), 7.3–8.1 ppm (m, 4 H, aryl protons); ir (KBr) 1590, 1325, 1140 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.38; H, 5.36; N, 5.75; S, 13.18. Found: C, 49.51; H, 5.36; N, 5.73; S, 13.07.

Nitronic Acid Methyl Ester from α-Nitrobenzyl *p*-Tolyl Sulfone (3). Yield 58%; mp 104.1–104.3° dec (from CH_2Cl_2–*n*-hexane); NMR ($CDCl_3$) δ 2.48 (s, 3 H, aryl CH_3), 3.68 (s, 3 H, OCH_3), 7.3–8.1 ppm (m, 9 H, aryl protons); ir (KBr) 1580, 1320, 1150 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95; N, 4.59; S, 10.50. Found: C, 59.01; H, 4.93; N, 4.58; S, 10.38.

Nitronic Acid Methyl Ester from Phenylsulfonylnitromethane (4). NMR ($CDCl_3$) δ 3.60, 3.62 (two singlets, 3 H, OCH_3), 6.78, 7.18 ppm (two singlets, 1 H, vinyl proton) (*E,Z* isomers, 1:1); ir (neat) 3100, 1600 cm^{-1} (vs. C=N).

Nitronic Acid Ethyl Ester from *p*-Tolylsulfonylnitromethane (5). NMR ($CDCl_3$) δ 0.9–1.3 (t, 3 H, CH_2CH_3), 3.9–4.3 (q, 2 H, CH_2CH_3), 7.02 ppm (s, 1 H, vinyl proton); ir (neat) 3100, 1600 cm^{-1} (vs. C=N).

Decomposition of the Nitronic Acid Esters 1–3. A solution of the appropriate, crude nitronic acid esters **1–3** (20 mmol) in 100 ml of CH_2Cl_2 was refluxed for 15 hr. Evaporation of the solvent in vacuo gave an oil. In the case of the decomposition of **1**, it was necessary to purify the residue by chromatography on silica gel, using a mixture of CH_2Cl_2 and EtOAc with increasing concentrations of EtOAc as the eluent. 3,4-Bis(*p*-tolylsulfonyl)furoxan was the only isolated product: yield 4.4%; mp 181.6–183.7° (from acetone–water; lit.[39] mp 183°, from acetone).

Upon decomposition of **2**, the residue was crystallized from benzene–*n*-hexane. Chromatography of the mother liquor on silica gel with CH_2Cl_2–EtOAc furnished another crop of α-(*p*-tolylsulfonyl)acetaldoxime: total yield 43%; mp 108.0–108.4° and 150° (from benzene; lit.[13] mp 97.1–97.6° and 146°).

Upon decomposition of **3**, the residue was crystallized from EtOAc–*n*-hexane: yield of α-(*p*-tolylsulfonyl)benzaldoxime 38%; mp 155° dec (from $CHCl_3$–*n*-hexane; lit.[13] mp 147.4° dec).

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