

INVESTIGATION OF RADICAL INTERMEDIATES IN ORGANIC REACTIONS BY USE OF NITROSO COMPOUNDS AS SCAVENGERS THE NITROXIDE METHOD

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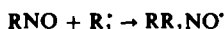
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Abstract—Hydrogen peroxide reactions with ketones were studied by the nitroxide method. Fragmentation of ketones proceeded *via* hydrogen peroxide adducts. Radical substitution took place with boranes and plumbanes. Postulated radicals from photolysis of certain ketones have been trapped. Photolysis of aryl iodides in the presence of *t*-nitrosobutane gave aromatic nitroxide radicals, the spectra of which were analyzed. Oxidative decarboxylation of carboxylic acid with thallic acetate proceeded *via* radicals. The splitting of the trichloromethyl nitroxide radicals is discussed. Some relationship between hyperfine splittings and structure has been observed.

INTRODUCTION

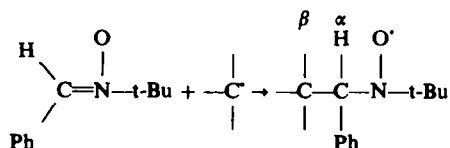
THE radical scavenging properties of nitroso compounds have been utilized for the study of radical intermediates of organic reactions.^{1-14a}



R_1 = alkyl, aryl, alkoxy, amide, acyl, alkylmercapto

The principles of the method are outlined in an earlier paper.⁷ In the following we shall refer to the method as the nitroxide method.* In order to minimize hyperfine couplings from the R moiety, which complicate the spectrum unnecessarily and also mask the splittings from the R group, *t*-nitrosobutane, I, and 2-nitrosobutanenone-3, II, were used as scavengers. In certain cases one or the other is preferable. A slight broadening of the lines caused by the hydrogens of the Me groups cannot be avoided ($a^{\text{H}} \leq 0.1 \text{ g}$).

A somewhat different approach utilizing a nitron as scavenger has been reported.¹⁵⁻¹⁹ This method suffers from the disadvantage that the hyperfine splittings of the radical are too small to be observed and so important information is lost. However, some radicals, e.g., $\text{RCOO} \cdot$, which we have not been able to trap with the nitroso compounds, have been detected by this method.



* The hydrogens of the α and β carbons with reference to the nitrogen atom are called α and β hydrogens.

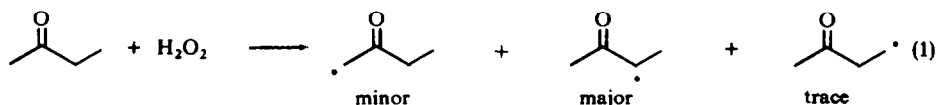
The fundamental problem of all reaction mechanistic studies is to decide whether a reaction is radical or ionic. We have here a new technique which is complementary to earlier methods. It ought to be impressed firstly that a negative result does not necessarily mean that radicals are not present, and secondly a positive result may well indicate a radical side reaction. With reference to the first point we have experienced that the radicals because of their rather capricious behaviour sometimes require very special trapping conditions. Temperature, solvent, irradiation, etc have to be carefully adjusted.

A quantitative estimation of different radical species in a mixture can only be made approximatively because all radicals are not scavenged with the same efficiency and the resulting nitroxides are not equally stable.

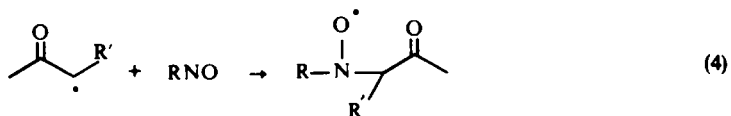
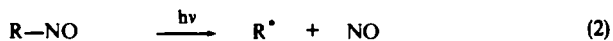
In the following sections examples of the use of the method are presented.

Reactions of ketones

Ketones and hydrogen peroxide. Hydroxyl radicals, generated by UV irradiation of hydrogen peroxide, attacked the ketones preferably in the α -position as was expected because resonance stabilized radicals were formed. As judged from the intensity of the nitroxide radicals, methylene hydrogens were more easily abstracted than methyl hydrogens.

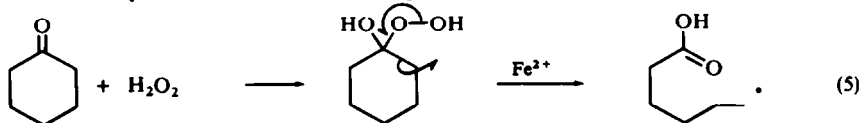


Traces of radicals could occasionally be detected when a solution of the nitroso compound in the ketone was irradiated in the absence of hydrogen peroxide. This was ascribed to the following sequence of reactions:



A similar mechanistic path was suggested by Mackor *et al.*² for a related reaction.

Ketones form adducts with hydrogen peroxide (5) from which in certain cases alkyl radicals were generated in a Fenton-type of reaction. The radical from cyclohexanone was used with success for synthetic purposes.²⁰ The fragmentation reaction (5) was easily demonstrated by use of the scavenger. Since iron ions caused a severe broadening of the lines, the peroxide bond was split by UV irradiation. The spectrum is shown in Fig 1. The two α -protons form a 1:2:1 triplet, $a^H = 10.5$ g, and the two β -protons



form a 1:2:1 triplet, $a^H = 0.57$ g. The three centre lines were masked by the symmetrical radical formed from the scavenger II, $[\text{CH}_3\text{COC}(\text{CH}_3)_2]_2\text{NO}\cdot$. Table 1 contains the ESR data for a number of ketone radicals.

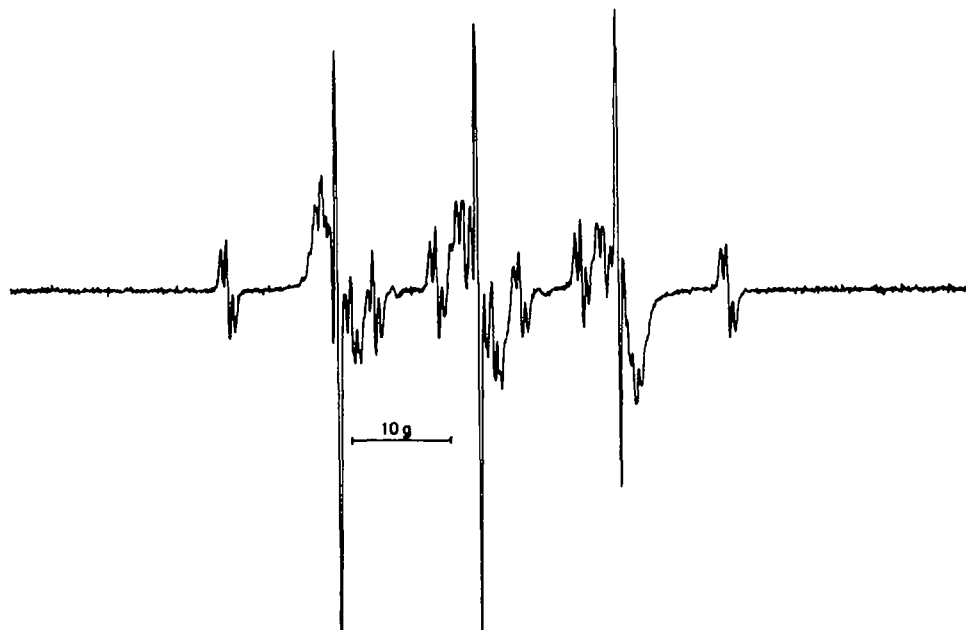
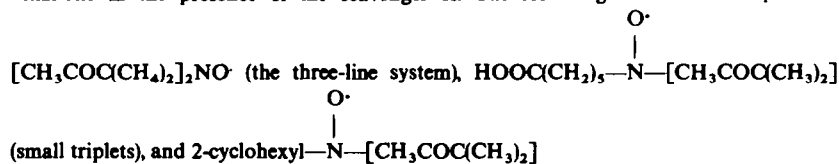
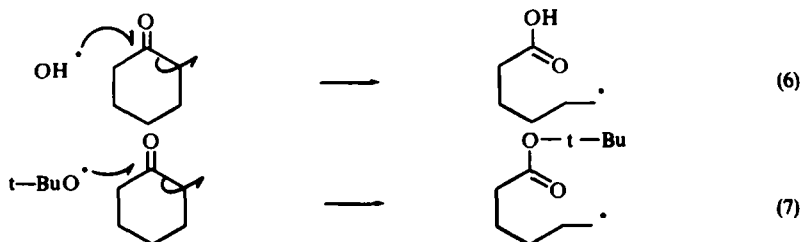


Fig 1. ESR-spectra of radicals obtained from the action of hydrogen peroxide on cyclohexanone in the presence of the scavenger II. The following nitroxides are present:

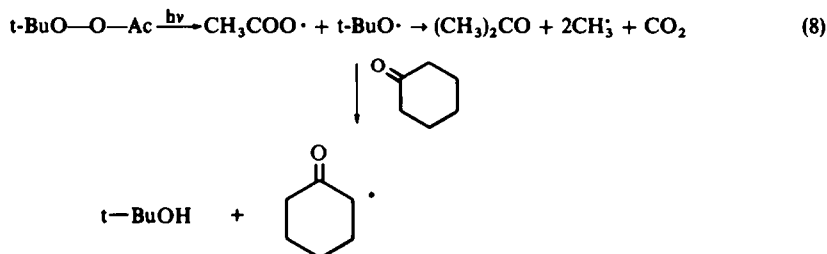


Somewhat unexpectedly, we could not detect the fragmentation radical from cyclopentanone in spite of the fact that it gave the corresponding synthetic products,²⁰ although in low yield. The radical formed by α -abstraction was detected and this intermediate was in fact used more successfully in another synthetic procedure.²¹ It should be possible to use the nitroxide method to map out conceivable synthetic schemes.

One could think of the radical substitution (6) as a mechanistic alternative to (5), in which the peroxide bond was preformed. In order to distinguish between the two possibilities

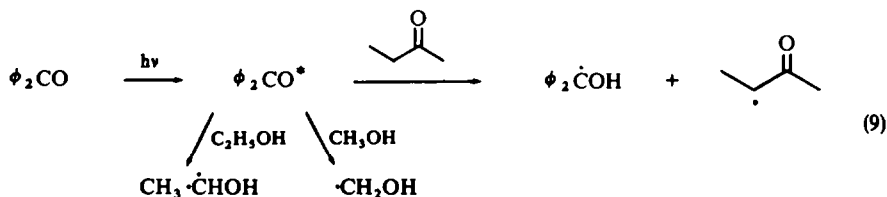


t-butylperacetate was photolyzed in cyclohexanone. In this case no peroxidic adduct could be formed and the only fragmentation route is *via* radical substitution (7). The ESR spectrum showed no trace of a ring opening reaction. The α -radical constituted the main product together with a small amount of Me radicals formed *via* (8).



Radical substitutions of type (6) are very seldomly met. The reaction will be discussed further in a following section.

Effects of sensitizer, photochemical reactions. No detectable amounts of radicals could be obtained in irradiation of 2-butanone in the absence of hydrogen peroxide, but addition of benzophenone immediately produced considerable amounts of the major radical, Table 1. Benzophenone, excited to its triplet state, is able to abstract hydrogens from suitable substrates (9) and the radicals formed were trapped by the



nitroso compounds. Alcohols were attacked in the position α to the OH group. Methanol [$a^N = 14.6$ g, $a^H = 5.1$ g (t)] and ethanol [$a^N = 14.9$ g, $a^H = 2.35$ (d)] gave the radicals depicted in (9) as was reported in a recent work^{14a} on the trapping of these radicals by the same technique. The alcohols were used as solvents in these reactions.

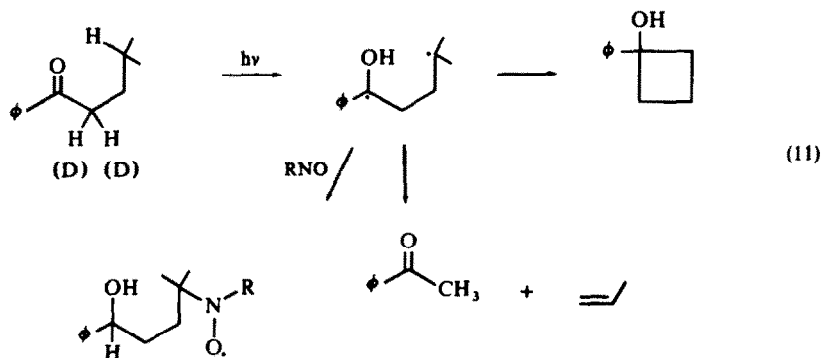
Irradiation of a series of phenyl alkyl ketones with increasing alkyl chain length in the presence of a scavenger demonstrates in a rather illuminating way some basic photochemical reactions of ketones. Methyl phenyl ketone and ethyl phenyl ketone give the α -radicals *via* intermolecular hydrogen abstraction (10), whereas the propyl and butyl derivatives give the γ -radicals *via* a 6-membered transition state (11). The



biradical has been postulated as an intermediate of the Norrish type II process.²²

Cyclisation afforded cyclobutane derivatives and olefine elimination methyl ketones (11). The latter reaction was also demonstrated by the finding that the ESR spectrum from irradiation of phenyl propyl ketone showed the presence of a less abundant radical showing the same hyperfine structure as the radical obtained from

acetophenone, i.e., ethylene must be eliminated according to (11). The intermediary radical was trapped and it exhibited the expected structure, Table 1. The radical from



phenyl butyl ketone showed a doublet of triplets, Fig 2. In this case the couplings from the β -hydrogens were too small to be resolved. In order to prove the γ -radical structure, the ketone was deuterated in the α -position and the radical from this sample showed the same structure.

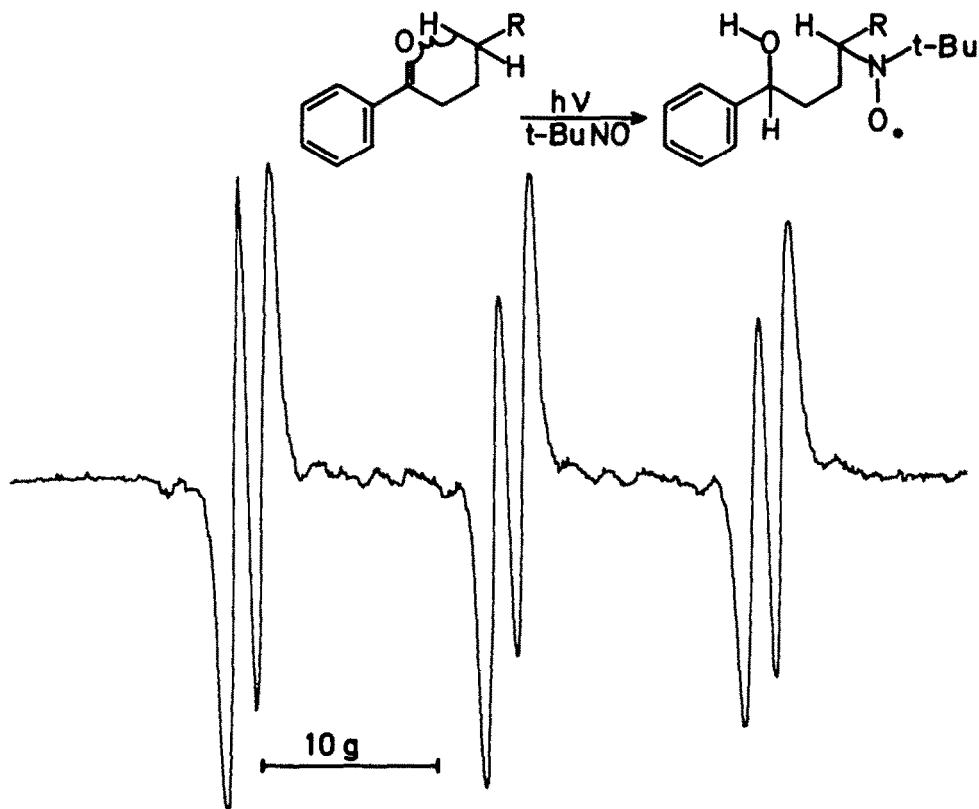



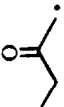
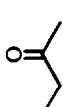

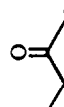
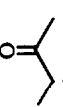
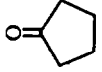
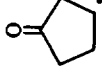
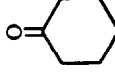
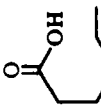
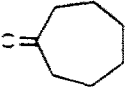
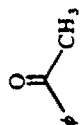
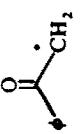
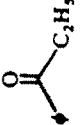
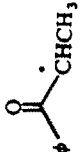
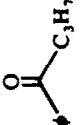
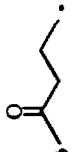
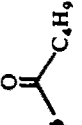

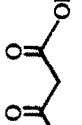
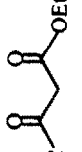
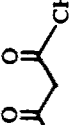
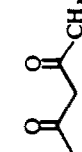




FIG 2. ESR-spectrum of the radical obtained by irradiation of *n*-butyl phenylketone in the presence of *t*-nitrosobutane

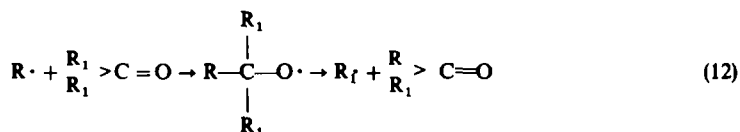
TABLE I. SPLITTING CONSTANTS OF NITROXIDE RADICALS DERIVED FROM KETONES
 THE KETONES SERVED AS SOLVENTS

Ketone	Scavenger	Intermediate radical	Temp. (°C)	$\alpha^N(g)$	$\alpha^H(g)$	$\alpha^H(g)$	Remarks
	$\begin{Bmatrix} \text{II} \\ \text{I} \end{Bmatrix}$		25	14.0	8.0(t)		14.1; 7.60 ⁷
	II	 (minor)	25	14.8	8.3(t)		
		 (major)	25	13.9	3.4(d)	0.3(g)	
	I	 (minor)	25	14.6	8.3(t)		
		 (major)	25	14.6	2.5(d)		
	II	 (major)	25	~14.3	~2.0(d)	~0.8(m)	no ring opening
	II	 mixture of rad. from H-abstr.	25	14.9	10.5(t)	0.57(t)	fragmentation
			25	14.4	~2.0(d)	~0.4(m)	

			II	mixture of rad. from H-abstr.	25	14.5	~2.0(d)	~0.4(m)	no ring opening			
			I		25	14.4	7.9(t)					
			{ I } { II }		25	14.5	5.2(d)					
			I		25	15.3	10.5(t)	0.5(t)	in CH ₂ Cl ₂			
			{ I } { II }		25	14.7	1.60(d)					
			II		25	13.9	7.8(t)					
			II		25	13.3	3.8(d)					
			II		25	13.2	3.53(d)					

Radical substitution

Radical addition to the carbonyl group is a rarely encountered process (12) in comparison to ionic addition, e.g., a Grignard reaction. The reverse fragmentation reaction is well known from radical chemistry, cf. (8). Furthermore, the hydrogen abstraction (3) competes favourably with (12) which makes it difficult to distinguish (12) from other reactions. Benzophenone was reacted with methyl radicals with the aim for forming acetophenone (12); ($R = \text{CH}_3$, $R_1 = \varphi$) or benzene but none of these compounds could be detected by GC. No phenyl radicals were detected by ESR



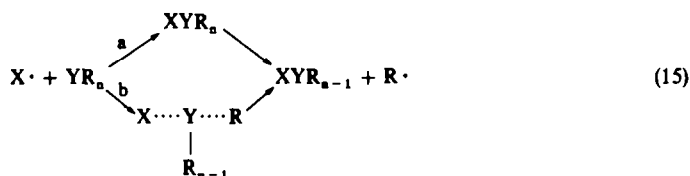
when *t*-butyl peracetate was photolysed at -60° in the ESR cavity in the presence of benzophenone and *t*-nitrosobutane as scavenger (12); $R = t\text{-BuO} \cdot$, $R_1 = \varphi$. It was reported that electron attracting groups attached to the keto function facilitated reaction (12).^{23,24} We therefore photolysed aqueous hydrogen peroxide in hexafluoroacetone but we were not successful in trapping the trifluoromethyl radicals.

However, by the nitroxide method some other similar radical substitutions have been demonstrated. Spontaneous decomposition of *t*-butylperoxalate (TBP)²⁵ in a solution containing lead tetraethyl gave ethyl radicals (13), and from the boranes²⁶ the corresponding radicals could be trapped by *t*-nitrosobutane (14). The nitroxide



R = phenyl, propyl

method has thus documented itself as a useful method for discovering new radical processes. We have not been able to decide whether (13), (14), and the DMSO reaction^{8,14} passes *via* a distinct intermediate (15a), or a transition state (15b).



A radical substitution at an sp^3 hybridized carbon, reaction b, $Y = \text{C}$, has up till now been reported in only one case²⁷ and in this area the nitroxide method could possibly give valuable contributions.

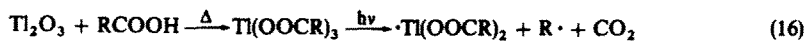
The trichloromethyl radical

From the reported a^N -values for bis-trifluoromethylnitroxide²⁸ (9.3 g), bis-trichloromethylnitroxide²⁹ (11.7 g), and di-*t*-butylnitroxide⁷ (15.85 g) one anticipates

for trichloromethyl-t-butyl nitroxide an a^N (splitting) of 13–14 gauss. The report¹⁰ of a value close to 7 gauss caused some doubts about the structure. A radical with this splitting was actually formed on photolysis of chloroform and carbon tetrachloride in the presence of t-nitrosobutane, but it also appeared in several other solvents. We therefore prepared nitrosotrichloromethane³⁰ with the intention of using this as a radical trap. The pure dark blue compound gave the earlier reported ESR spectrum for bis-trichloromethyl nitroxide, $a^N = 11.7$ g, $a^{Cl} = 1.25$ g. Very complicated spectra were obtained when nitrosotrichloromethane was used as a scavenger for the radicals generated by $\cdot\text{OH}$ with different organic compounds. The 7 gauss radical was, indeed, detected but so were radicals with a main triplet splitting of around 12 g which were heavily masked by bis-trichloromethyl nitroxide. In one experiment a mixture of nitroso trichloromethane and t-nitrosobutane was irradiated for a short time with UV light. Immediately after the light was switched off, a spectrum was visible, $a^N \sim 12$ g, $a^{Cl} = 2.5$ g, on top of which the bis-trichloromethyl nitroxide spectrum rapidly developed. At that point the work by Leaver *et al.*¹³ on the trapping of trichloromethyl radicals appeared which solved the problem; $a^N = 12.73$ g, $a^{Cl} = 2.41$ g for t-butyl trichloromethyl nitroxide. The origin of the 7 gauss radical remains unclear but the splitting indicates an acyl radical.

Oxidative decarboxylation with Ti^{3+}

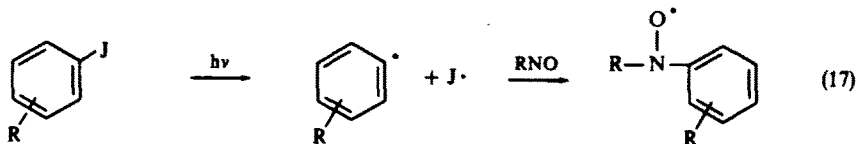
The intermediary appearance of radicals in oxidative decarboxylation by lead tetraacetate was demonstrated by the nitroxide method.⁷ Irradiation of thallic carboxylates at -50° gave, according to (16), the corresponding alkyl radicals which were scavenged by t-nitrosobutane. The lines were broadened as a result of interaction



between the nitroxide and the thallic ions. The hyperfine structure from the Me group in the Et group could not be resolved. Kochi *et al.*³¹ have recently by synthetic methods shown the intermediary formation of radicals. Irradiation of thallic trifluoroacetate produced trifluoromethyl radicals, which were trapped by t-nitrosobutane, $a^N = 12.2$ g, $a^F = 12.5$ g (CH_2Cl_2 , -60°C).

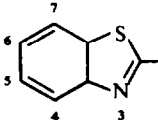
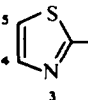
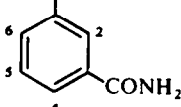
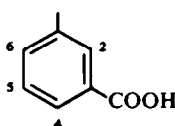
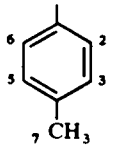
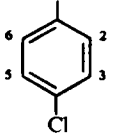
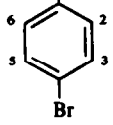
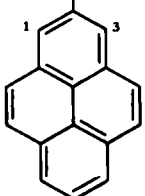
Homolytic fission of aryl iodides

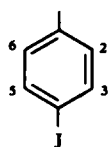
Irradiation of aryl iodides in aromatic solvents gives diaryls in good yields.³² The formation of aryl radicals can be demonstrated by the nitroxide method and this way of generating aromatic nitroxide radicals seems to be a convenient and general method (17). In Table 2 the ESR data are collected. A few heteroaromatic compounds



are also included. Figure 3a depicts the spectrum obtained from 2-iodothiazole together with the simulated spectrum. The spin density as calculated by HMO methods is in agreement with simple resonance structures, cf. Table 2. An *ortho*-substituent rotates the ring out of the plane of the nitroxide group decreasing the conjugation

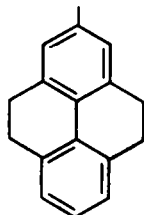
TABLE 2. SPLITTING CONSTANTS OF AROMATIC NITROXIDE RADICALS
 Ar-NO-t-Bu, IN METHYLENE CHLORIDE, -60°

Ar	Splitting constants, gauss	
	$a^N(>NO\cdot)$	Other nuclei
	9.33	$a^{N3} = 2.65, a^{H4} = a^{H6} = 1.32, a^{H5} = a^{H7} \sim 0$
	9.90	$a^{N3} = 2.35, a^{H4} = 0.48, a^{H5} = 3.15$
	12.6	$a^{H2} = a^{H4} = a^{H6} = 1.99, a^{H5} = 0.98$
	12.6	$a^{H2} = a^{H4} = a^{H6} = 1.95, a^{H5} = 0.90$
	13.0	$a^{H2} = a^{H6} = a^{H7} = 2.00, a^{H3} = a^{H5} = 0.92$
	12.4	$a^{H2} = a^{H6} = 2.1, a^{H3} = a^{H5} = 1.0$
	12.3	$a^{H2} = a^{H6} = 2.16, a^{H3} = a^{H5} = 1.08$
	12.8	$a^{H1} = a^{H3} = 2.18^a$



12:1

$$a^{H_2} = a^{H_3} = 2.1, a^{H_4} = a^{H_5} = 1.0$$

~12.2^b

2-tolyl	14.0 ^c
2-carboxyphenyl	14.7 ^c
2,4,5-tribromophenyl	13.9 ^c
2-chloro-4-bromophenyl	13.8 ^c

^a The other splittings could not be resolved.

^b Very broad band.

^c The ring is out of the plane, broad line.

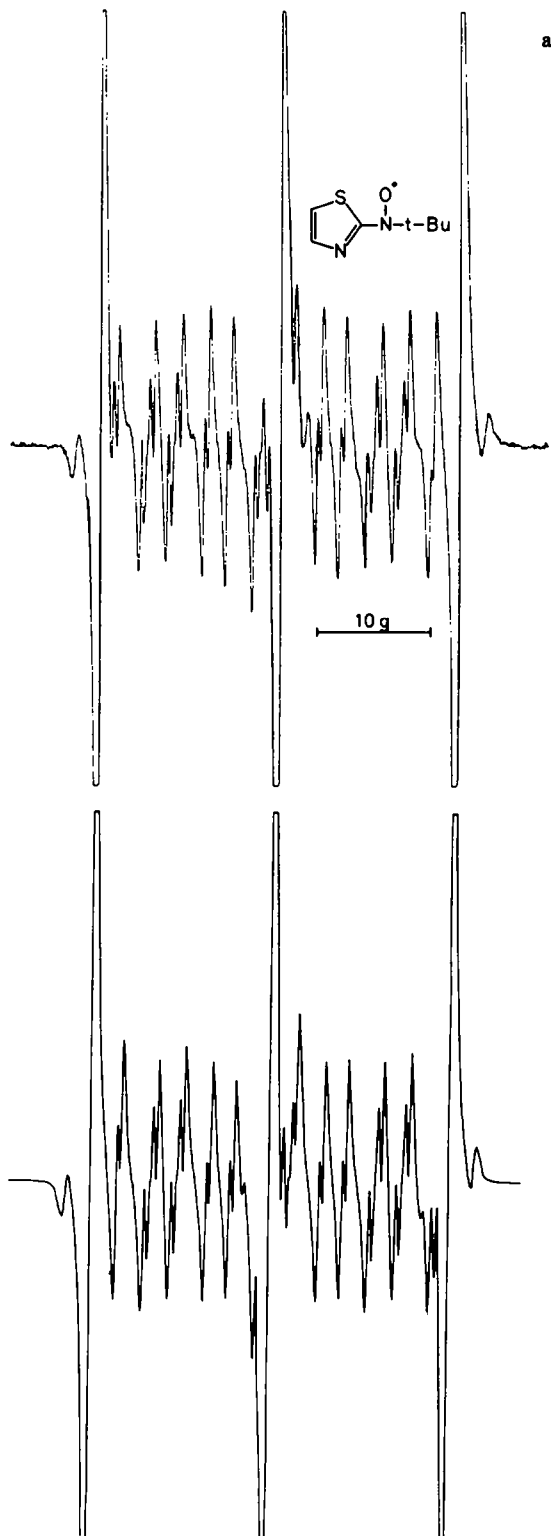
with the nitroxide group. This was reflected in the ESR spectra as an increased a^N splitting and a diminished coupling with the ring protons; e.g. *o*-carboxamidophenyl-*t*-butyl nitroxide gave only the central triplet, $a^N = 13.9$ g, with line width broadening. Barbarella and Rassat³³ have prepared a series of nitroxide radicals by reacting Grignard compounds with nitro derivatives and their measurements are in good agreement with our ESR data.

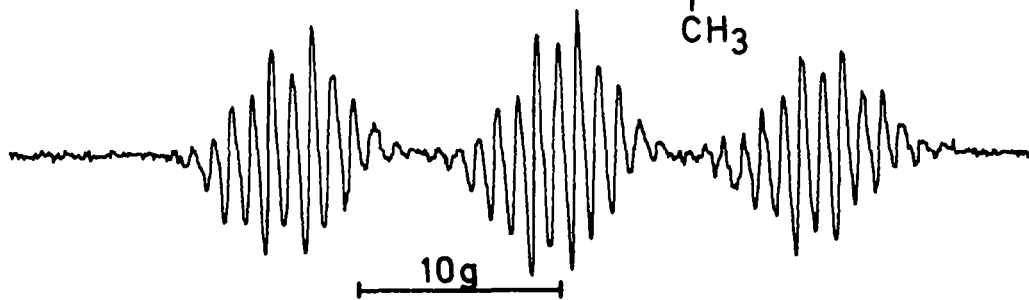
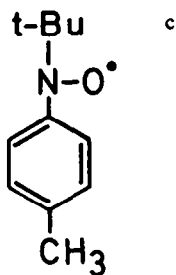
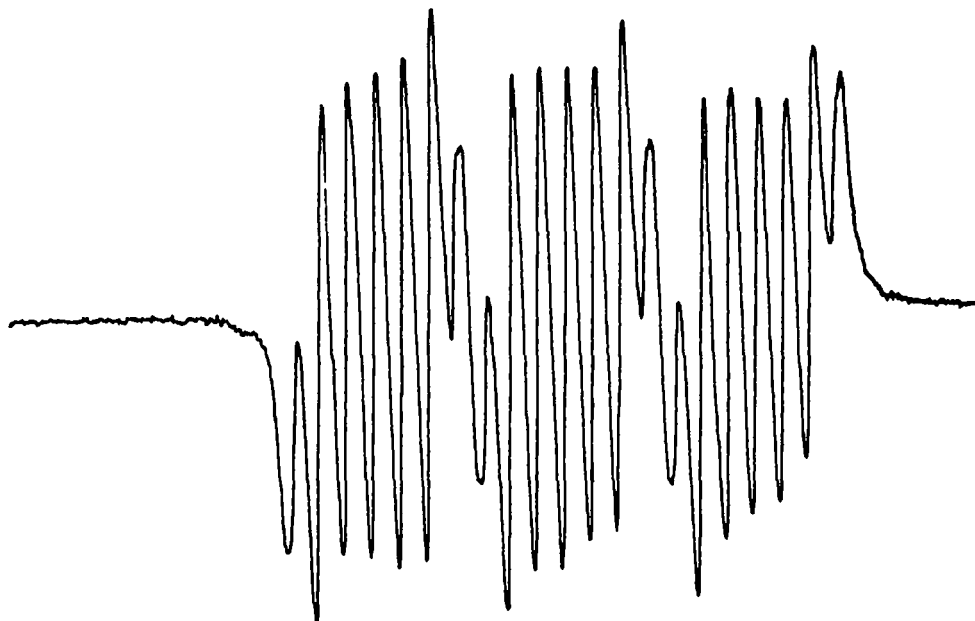
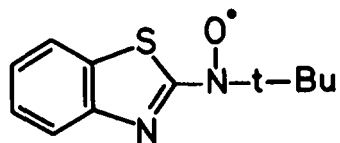
2-Iodopyrene gave rise to a spectrum consisting of a somewhat broadened triplet (2H) of triplets (1N), indicating a comparatively high spin density on the two *ortho*-carbons and a small density on all the other carbons. HMO calculations showed in fact that the density at the 1- and 3-positions is 5–6 times higher than at any other position (C₇). The 4, 5, 9, 10-tetrahydro derivative has a much more uniform electron distribution; broad lines were obtained which could not be resolved.

Relations between hyperfine splittings and structure

The splitting constant, a^N , depends on the nature of R and R' of the nitroxides.^{7, 34} However, minor structural changes within the groups induced small, but significant changes. These changes amounted to a few gauss at the most and since solvent effects^{7, 35} were of the same order of magnitude, it was necessary to make comparative measurements in the same solvent. Data found in the literature refer to a variety of solvents, and for various reasons the present measurements had to be carried out in different media, but nevertheless, it appeared that α -substituent effects could be accounted for in a predictable way.

If we consider a series of aliphatic nitroxides with an increasing number of α -keto





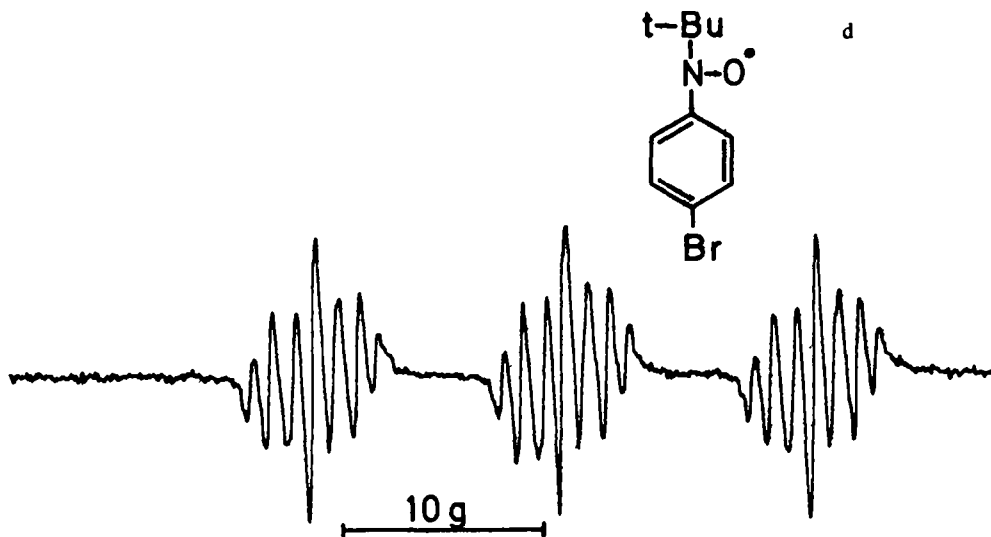


FIG 3. ESR-spectra of aryl-t-butyl nitroxides. 3a also shows the simulated spectrum

groups, we find that the a^N splitting decreases: no CO, 15.8 ± 0.5 g; 1 CO, 14.9 ± 0.5 g; 2 CO, 14.1 ± 0.5 g; 3 CO 13.4 ± 0.5 g; 4 CO, 12.9 ± 0.5 g. These numbers refer to solvents of medium polarity, e.g., methylene chloride. In water the a^N -values were ca. 1–2 gauss higher and in benzene somewhat lower, ca. 0.2 gauss. Other electron attracting groups had the same lowering effect, e.g., phenyl, hydroxy, alkoxy groups. The two last mentioned groups had the same inductive effect as a carbonyl group. It seems to be possible from the values presented to distinguish between alkyl radicals and α carbonyl substituted alkyl radicals. A more detailed investigation of a number of structures in the same solvent and with a standard R group, e.g., t-butyl, is desirable.

The α -alkyl methylene and α -acyl methylene protons gave characteristic triplet splittings of ca. 10.5 and 8 gauss, respectively. The doublet splitting from a methine proton is smaller, 1.5–6 gauss. The splittings from β -hydrogens are small, ≤ 0.7 gauss, and could in many cases not be resolved.

EXPERIMENTAL

The ESR measurements were recorded with a Varian E 3 instrument. A flat cell was used inserted in a variable temp accessory.

2-Methyl-2-nitrosobutanone-3,³⁶ t-nitrosobutane,³⁷ t-butylperoxalate,²⁵ nitroso trichloromethane,³⁰ propyl-phenylketone,³⁸ and butyl-phenylketone³⁸ were prepared according to the literature. Ketones, iodides, and other compounds used were commercial preparations.

The ketonic radicals were prepared by dissolving a few crystals, 0.1–1 mg of the scavenger, and adding a small drop of 30% H_2O_2 or t-butylperoxide to 0.5 ml of the ketone. The sample was irradiated by light from a high pressure Hg lamp, 500 W, filtered by $CuSO_4$ soln, ca. 1 M. Spectra were recorded at various times of irradiation and at various temps. The radicals had a limited life-time. The solns used were not de-aired. The spectra could be recorded practically immediately.

The iodides, ca. 50 mg, were dissolved in CH_2Cl_2 (0.5 ml), and a few crystals of t-nitrosobutane were added. The soln was irradiated at -60° and in most instances the spectra could be recorded after a few min.

The Et radicals from lead tetraethyl were formed by dissolving it in CH_2Cl_2 -AcOH together with di t-butylperoxalate and the scavenger. The peroxalate decomposed spontaneously at room temp and after a short time, the ethylnitroxide was formed. Triphenylborane and tripropylborane were irradiated in CH_2Cl_2 soln with scavenger and t-butylperacetate at -60° and $+25^\circ$, respectively. No radicals were formed without the peroxide present.

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