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Spin Trapping of Free Radicals Generated from Arylazo *p*-Tolyl Sulfones[1]

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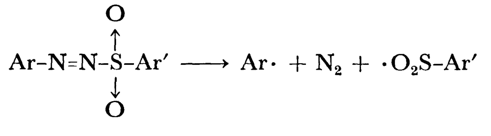
Arylazo *p*-tolyl sulfones(I) were thermolyzed or photolyzed in the presence of trapping agents such as α,*N*-diphenyl nitrone(II), α-phenyl *N*-*t*-butyl nitrone(III) and 2-methyl-2-nitrosopropane(X). ESR studies showed that phenyl radical or *p*-methoxyphenyl radical is produced from the decomposition of I and adds to II or III. The adduct of phenyl radical to II and that of *p*-methoxyphenyl radiacl to III were synthesized for comparison by separate pathways. The photolysis of phenyl *p*-tolylazo sulfone(Ia) in the presence of III yielded benzhydryl *t*-butyl nitroxide, benzoyl *t*-butyl nitroxide and *t*-butyl *p*-toluenesulfonyl nitroxide(XVI) radicals. The photolysis of Ia in the presence of X gave di-*t*-butyl nitroxide(XII) and XVI. The photolysis of phenylazotriphenylmethane in the presence of X yielded XII and *t*-butyl nitroxide radical. The mechanisms of the formation of these radicals are discussed. The formation of arenesulfonyl radicals from the decomposition of I has been proved indirectly (analyses of the products of the combination of nitroxide radicals with arenesulfonyl radicals) and directly (detection of *t*-butyl *p*-toluenesulfonyl nitroxide radical).

Arylazo *p*-tolyl sulfones(I) decompose when they are heated in neutral or weakly basic media[2] or when they are irradiated by UV light,[3] and the generation of aryl radicals has been proposed on the basis of kinetic studies[4] or product studies (orientation and partial rate factors in arylating various aromatics).[5]



$$\text{Ar-N=N-}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{-Ar}' \longrightarrow \text{Ar}\cdot + \text{N}_2 + \cdot\text{O}_2\text{S-Ar}'$$

(I)

Ia: Ar=Ph, Ar′=*p*-Tolyl
Ib: Ar=*p*-MeO-C_6H_4, Ar′=*p*-Tolyl

However, no evidence has been presented indicating the formation of arenesulfonyl radicals, since they do not attack aromatics easily.[6,7] Consequently, mechanisms involving only aryl radicals (*i. e.*, not arenesulfonyl radicals) cannot be excluded. A plausible example is the following mechanism, which is similar to the diazoanhydride–acetic anhydride mechanism proposed for the decomposition of N-nitrosoacetanilide by Rüchardt *et al.*[8]

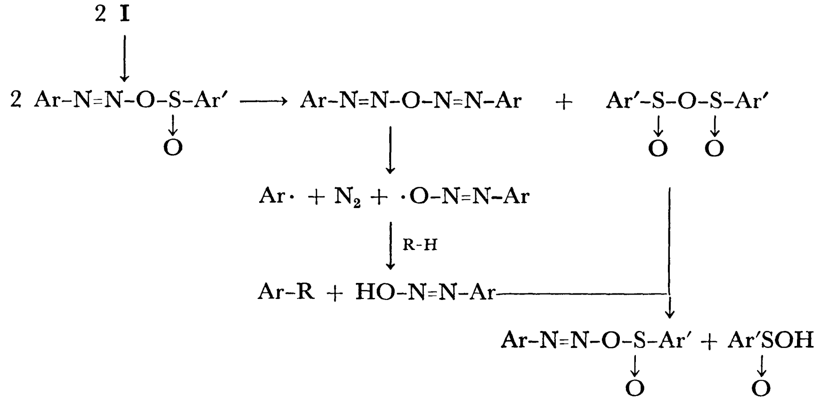
Even the formation of aryl radicals from I has not been proved by physical methods. Spin trapping of aryl and arenesulfonyl radicals has therefore been investigated, and the results are descirbed in this paper.

Results and Discussion

When benzene solutions of phenylazo *p*-tolyl sulfone (Ia) or *p*-methoxyphenylazo *p*′-tolyl sulfone (Ib) were heated or irradiated, ESR spectra did not indicate the presence of aryl radicals. The reactivities of aryl radicals are probably so great that the steady-state concentrations of aryl radicals produced are not large enough for ESR detection.

Trappings[9] of aryl radicals by reactions with α,*N*-diphenyl nitrone (II) or α-phenyl *N*-*t*-butyl nitrone (PBN) (III) were attempted. When benzene solutions of Ia and II (or Ib and II) were mixed at room temperature in the dark, ESR signals were observable. This indicates that free radicals are slowly produced by thermolysis of Ia or Ib at room temperature. When these mixtures were irradiated with a 100-W high pressure mercury lamp, very strong ESR signals composed of 40 hyperfine splittings (shown in Fig. 1a) were observed. The ESR signal patterns of the radicals produced by photolysis were the same as those observed for the radicals produced by thermolysis at room temperature. Thus, the radicals produced by photolysis and thermolysis should be the same.

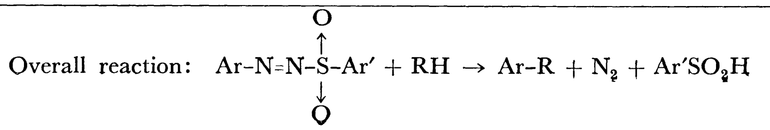
The following hyperfine splitting constants were cal-



$$2\,\text{Ar-N=N-O-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Ar}' \longrightarrow \text{Ar-N=N-O-N=N-Ar} + \text{Ar}'\text{-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-O-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Ar}'$$

$$\text{Ar}\cdot + \text{N}_2 + \cdot\text{O-N=N-Ar} \xrightarrow{\text{R-H}} \text{Ar-R} + \text{HO-N=N-Ar}$$

$$\text{Ar-N=N-O-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Ar}' + \text{Ar}'\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{OH}$$



$$\text{Overall reaction: Ar-N=N-}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{-Ar}' + \text{RH} \rightarrow \text{Ar-R} + \text{N}_2 + \text{Ar}'\text{SO}_2\text{H}$$

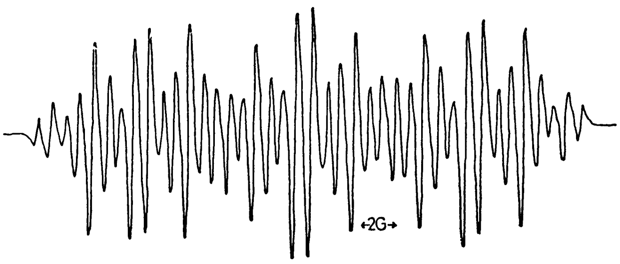


Fig. 1(a). The ESR spectrum of an irradiated mixture of $p\text{-MeOC}_6\text{H}_4\text{N=NO}_2\text{SC}_6\text{H}_4\text{Me-}p$ and $\mathrm{PhCH{=}\underset{\downarrow \atop O}{N}\text{-}Ph}$ in benzene.

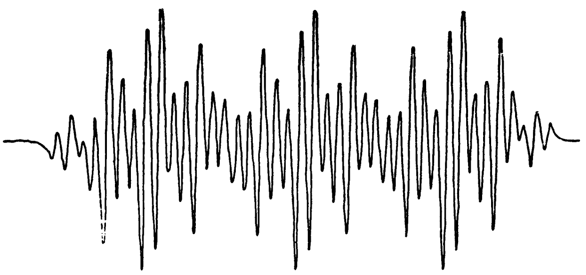


Fig. 1(b). An ESR spectrum obtained by simulation using $A_\text{N}=10.01$, $A_{\beta\text{-H}}=3.41$, $A_{o\text{-H}}=2.51$, $A_{m\text{-H}}=0.88$, and $A_{p\text{-H}}=2.51\text{G}$.

culated from analysis of the hyperfine splittings.

$A_\text{N} = 10.01$

$A_{\beta\text{-CH}} = 3.41$

$A_{o\text{-H}} = 2.51$

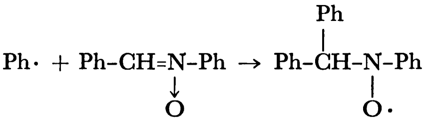
$A_{m\text{-H}} = 0.88$

$A_{p\text{-H}} = 2.51$

$g = 2.0056$

Simulation was carried out by using these hyperfine splitting constants, the result (Fig. 1b) being in excellent agreement with what was experimentally observed. Thus the radical responsible for the ESR pattern is benzhydryl phenyl nitroxide radical (IVa) shown below.

$$\text{Ia} \longrightarrow \text{Ph}\cdot$$

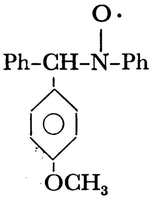


$$\mathrm{Ph\cdot + Ph\text{-}CH{=}\underset{\underset{O}{\downarrow}}{N}\text{-}Ph \rightarrow Ph\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{O\cdot}{|}}{N}\text{-}Ph}$$

(II) (IVa)

Bluhm and Weinstein[10] trapped the phenyl radical, produced from phenylazotriphenylmethane, by the reaction with II, and the hyperfine splitting constants they reported for radical IVa are approximately the same as those described above.

When Ib was decomposed by irradiation or by heating in the presence of II, ESR signals ascribable to nitroxide radical IVb were observed. The following hyperfine splitting constants were obtained from the analysis of the ESR pattern.



(IVb)

$A_\text{N} = 10.0$

$A_{\beta\text{-H}} = 3.4$

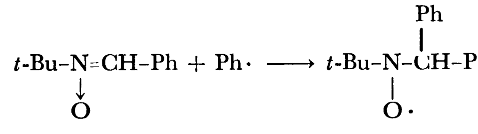
$A_{o\text{-H}} = 2.5$

$A_{m\text{-H}} = 0.9$

$A_{p\text{-H}} = 2.5$

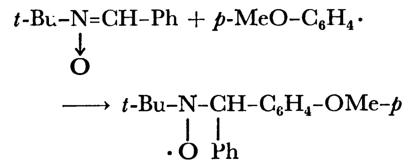
When the samples were irradiated at room temperature and the ESR signals were examined after the light was turned off, they were observable for about 15 min. This indicates that radicals IVa and IVb are fairly stable.

ESR studies on the reaction between Ia and nitrone III and that between Ib and III showed the presence of nitroxide radicals Va and Vb, respectively. The following hyperfine splitting constants were obtained.



$$\mathrm{\text{t-}Bu\text{-}\underset{\underset{O}{\downarrow}}{N}{=}CH\text{-}Ph + Ph\cdot \longrightarrow \text{t-}Bu\text{-}\underset{\underset{O\cdot}{|}}{N}\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}Ph}$$

(III) (Va)



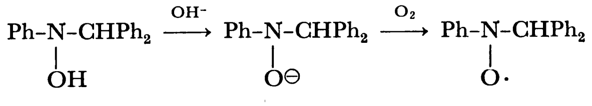
$$\mathrm{\text{t-}Bu\text{-}\underset{\underset{O}{\downarrow}}{N}{=}CH\text{-}Ph + \text{p-}MeO\text{-}C_6H_4\cdot \longrightarrow \text{t-}Bu\text{-}\underset{\underset{\cdot O}{|}}{N}\text{-}\underset{\underset{Ph}{|}}{C}H\text{-}C_6H_4\text{-}OMe\text{-}p}$$

(Vb)

	A_N	$A_{\beta\text{-CH}}$	g
Va	13.93	2.09	
Vb	13.91	2.15	2.0061

Concerning Va, Janzen and Blackburn reported that $A_\text{N}=13.73$ and $A_{\beta\text{-CH}}=2.08$ G.[11]

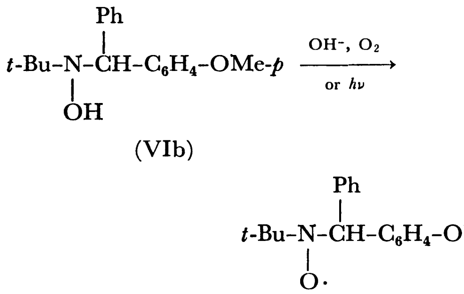
In order to prove the structure of IVa, *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was synthesized from nitrone II and phenylmagnesium bromide, and was oxidized with air in a weakly alkaline (NaOH) aqueous ethanol. The ESR signals observed were exactly the same as those observed when Ia was photolyzed in the presence of II. When VIa was treated with *n*-BuLi in benzene and then irradiated with a high pressure mercury lamp in the presence of air, similar ESR signals ascribable to nitroxide radical IVa were observed.



$$\mathrm{Ph\text{-}\underset{\underset{OH}{|}}{N}\text{-}CHPh_2 \xrightarrow{OH^-} Ph\text{-}\underset{\underset{O^\ominus}{|}}{N}\text{-}CHPh_2 \xrightarrow{O_2} Ph\text{-}\underset{\underset{O\cdot}{|}}{N}\text{-}CHPh_2}$$

(VIa) (IVa)

In a similar manner, when an alkaline ethanol solution of *N*-*t*-butyl-*N*-(phenyl-*p*-methoxyphenylmethyl)hydroxylamine (VIb) was oxidized with air or irradiated in the presence of air, nitroxide radical Vb was formed and its ESR signals were identical with those obtained from azosulfone Ib and nitrone III.

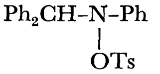


$$\mathrm{\text{t-}Bu\text{-}\underset{\underset{OH}{|}}{N}\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}C_6H_4\text{-}OMe\text{-}p \xrightarrow[\text{or } h\nu]{OH^-,\ O_2} \text{t-}Bu\text{-}\underset{\underset{O\cdot}{|}}{N}\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}C_6H_4\text{-}OMe\text{-}p}$$

(VIb) (Vb)

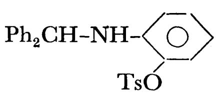
These data obtained by means of ESR have established that aryl free radicals are formed by thermolysis or photolysis of azosulfones Ia or Ib.

In order to determine the final products from nitroxide radicals IV and V, a mixture of Ia, pyridine (3 mol/mol Ia; added in order to keep the medium weakly alkaline) and nitrone II (1.5 mol/mol Ia) was thermolyzed. Recrystallization of the products gave a compound, which appeared to be *N*-benzhydryl-*N*-phenylhydroxylamine *O*-*p*-toluenesulfonate (VII). It was very unstable, readily isomerizing to *o*- and *p*-benzhydrylaminophenyl *p*-toluenesulfonates (VIII) and (IX), when allowed to stand at room temperature. When the products of thermolysis of Ia-II-pyridine in benzene were separated by column chromatography, VII was not detected and VIII and IX were isolated in 17% and 1% yields (per 100 mol Ia), respectively.

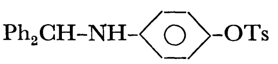


$Ph_2CH\text{-}N(OTs)\text{-}Ph$

(VII)

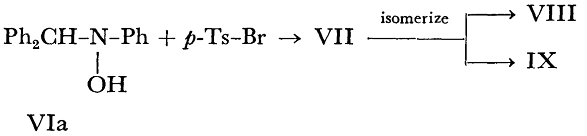


(VIII)



(IX)

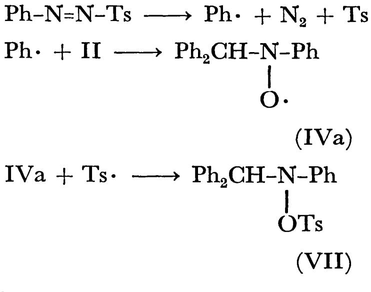
When *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was allowed to react with *p*-tosyl bromide in pyridine at room temperature, VII was not obtained; isomerization took place during the course of recrystallization and the product isolated was VIII. A similar rearrangement of hydroxylamine-O-esters has been reported.[12]



$Ph_2CH\text{-}N(OH)\text{-}Ph + p\text{-}Ts\text{-}Br \rightarrow VII \xrightarrow{\text{isomerize}} VIII,\ IX$

VIa

The formation of VII can be ascribed to a combination of nitroxide radical IVa and *p*-toluenesulfonyl radical.



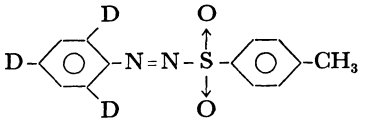
$$Ph\text{-}N{=}N\text{-}Ts \longrightarrow Ph\cdot + N_2 + Ts\cdot$$
$$Ph\cdot + II \longrightarrow Ph_2CH\text{-}N(O\cdot)\text{-}Ph \quad (IVa)$$
$$IVa + Ts\cdot \longrightarrow Ph_2CH\text{-}N(OTs)\text{-}Ph \quad (VII)$$

The fact that VII is formed proves indirectly that the decomposition of azosulfone Ia yields *p*-toluenesulfonyl radical in addition to phenyl radical.

In an attempt to trap *p*-tosyl radical with nitrone III, Ia was photolyzed in the presence of excess III at room temperature under various conditions. The presence of two new nitroxide radicals in addition to Va were detected by ESR; $A_N=12.5$ G and 7.67 G (for Va, $A_N=13.93$ G). Since these two radicals showed simple triplets without hyperfine splittings due to β-hydrogens, addition of radicals on some nitroso compounds containing only *t*-butyl groups was suspected. When an ethereal solution of Ia was irradiated at 366 nm in the presence of 2-methyl-2-nitrosopropane(X), ESR signals of two radicals were observed; $A_N=12.5$ G and 15.5 G, and $g=2.0060$ for both. In order to determine whether or not these radicals arose from trapping of phenyl radical, *p*-tolyl 2,4,6-trideuteriophenylazo sulfone (Ia-d_3) was photolyzed in the presence of X. Since the radicals detected were identical with those formed in the case of Ia, they cannot be the products of trapping of phenyl radical with X.

$(CH_3)_3C\text{-}N{=}O^\cdot$

(X)

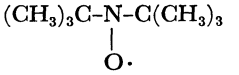


(Ia-d_3)

When phenylazotriphenylmethane (XI), another phenyl radical source, was photolyzed in ether in the presence of X, two radicals were detected; one with $A_N=12.8$ G and $A_{\beta\text{-CH}}=2.6$ G and the other with $A_N=15.5$ G. When X was irradiated in ether with a sodium lamp (589 nm), the ESR signals obtained were a simple triplet with $A_N=15.5$ G. Therefore, the radical with $A=15.5$ G must be di-*t*-butyl nitroxide radical (XII).

$Ph\text{-}N{=}N\text{-}CPh_3$

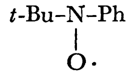
(XI)



$(CH_3)_3C\text{-}N(O\cdot)\text{-}C(CH_3)_3$

(XII)

It has been reported that XII is formed by the photolysis of X; $A_N=15.7$ G[13] or 15.5 G,[14] and also that *t*-butyl phenyl nitroxide (XIII) formed by the trapping of phenyl radical with X shows hyperfine splittings due to *ortho* and *para* hydrogens of the benzene ring.[13,14]



$t\text{-}Bu\text{-}N(O\cdot)\text{-}Ph$

(XIII)

$A_N=12.4,^{13)}\ 13.3G^{14)}$

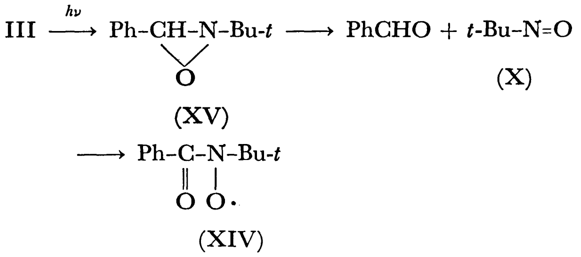
$A_{o\text{-H}}=2.0,^{13}\ 1.8^{14)}$

$A_{m\text{-H}}=0.9,\ 0.9$

$A_{p\text{-H}}=2.0,\ 1.8$

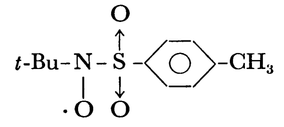
The fact that no XIII was found in the photolysis of Ia in the presence of X can be ascribed to the consumption of phenyl radical by abstraction of α-hydrogens of ether.

The radical with $A_N=7.67$ G formed in the photolysis of Ia in the presence of III is probably benzoyl *t*-butyl nitroxide radical[11] (XIV) produced by the photolysis of III. It has been reported[15] that upon irradiation nitrone III isomerizes to α-phenyl-*N*-*t*-butyloxazirane (XV), which then yields 2-methyl-2-nitrosopropane (X) and XIV.



$$III \xrightarrow{h\nu} Ph\text{-}CH\text{-}N\text{-}Bu\text{-}t\ (XV) \longrightarrow PhCHO + t\text{-}Bu\text{-}N{=}O\ (X)$$
$$\longrightarrow Ph\text{-}C({=}O)\text{-}N(O\cdot)\text{-}Bu\text{-}t \quad (XIV)$$

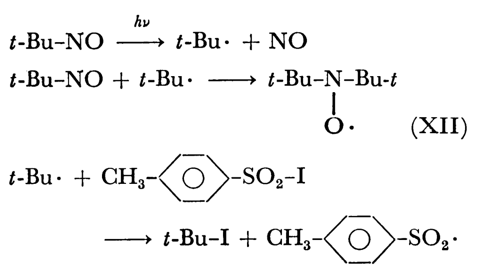
Thus, of the three radicals produced from the photolysis of Ia in the presence of III, the one with $A_N=13.93$G is Va, that with $A_N=7.67$ G is XIV, and that with $A_N=12.5$ G remains to be explained. If this is not XIII, the only possibility seems to be nitroxide radical XVI, which can be formed by the trapping of *p*-toluenesulfonyl radical with X. In order to confirm the



(XVI)

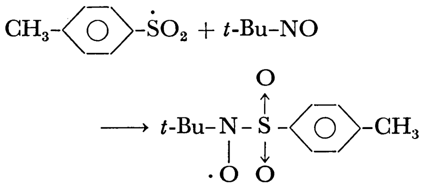
possibility, *p*-toluenesulfonyl iodide, another *p*-tosyl radical source, was irradiated at 589 nm in the presence of X. A nitroxide radical with $A_N = 12.5$ G was observed, which is identical with that obtained in the photolysis of Ia or Ib in the presence of X.

The rate of decrease of the ESR signals of XVI was determined after light was turned off, and the nitroxide radical XVI was found to be a fairly stable radical with a half-life of 44 seconds. When an ethereal solution of X was irradiated in the absence of *p*-tosyl iodide, ESR signals observed were those of di-*t*-butyl nitroxide (XII) alone. The following reaction sequence is therefore plausible.

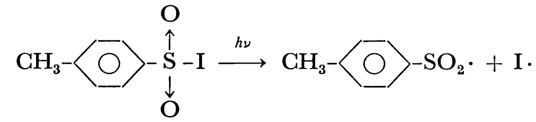


$$t\text{-Bu-NO} \xrightarrow{h\nu} t\text{-Bu}\cdot + \mathrm{NO}$$

$$t\text{-Bu-NO} + t\text{-Bu}\cdot \longrightarrow t\text{-Bu-}\underset{\substack{|\\ \mathrm{O}\cdot}}{\mathrm{N}}\text{-Bu-}t \quad \text{(XII)}$$



It is possible that *p*-toluenesulfonyl radical is produced by direct photolysis of *p*-toluenesulfonyl iodide itself.[6)]



However, since X absorbs at longer wavelength region (near 589 nm), it seems more probable that the *t*-butyl radical produced by photolysis of X abstracts the iodine atom from *p*-tosyl iodide, yielding *p*-tosyl radical and *t*-butyl iodide.

When an ethereal solution of iodobenzene was irradiated in the presence of X, two sets of ESR signals were observed; a triplet with $A_N = 15.5$ G and a triplet with $A_N = 12.5$ G and with hyperfine splittings. The former is due to XII, and the latter can be ascribed to *t*-butyl phenyl nitroxide (XIII). The formation of XIII can be explained in terms of the following reaction steps: 1) photolysis of X gives *t*-butyl radical, 2) *t*-butyl radical abstracts the iodine atom from iodobenzene, and 3) the phenyl radical formed is trapped

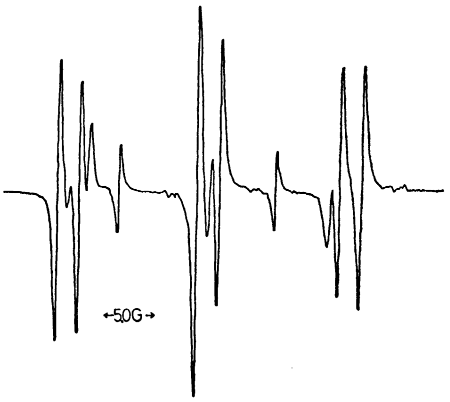


Fig. 2(a). The ESR spectrum of an irradiated mixture of $\mathrm{PhN{=}NO_2SC_6H_4\text{-}Me\text{-}}p$ and $t\text{-Bu-}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{N}}\text{=CH-Ph}$ in benzene ($A_N = 13.13$, $A_{\beta\text{-H}} = 2.09$; $A_N = 12.5$; $A_N = 7.67$G).

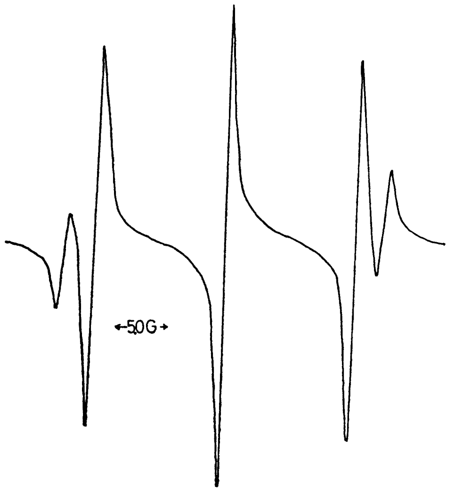


Fig. 2(c). The ESR spectrum of an irradiated mixture of $\mathrm{PhN{=}NO_2SC_6H_4Me\text{-}}p$ and t-Bu-N=O in ether ($A_N = 12.5$, and $A_N = 15.5$G).

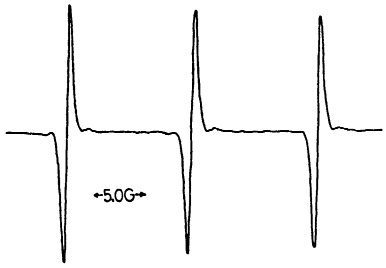


Fig. 2(b). The ESR spectrum of an irradiated solution of t-Bu-N=O in ether ($A_N = 15.5$G).

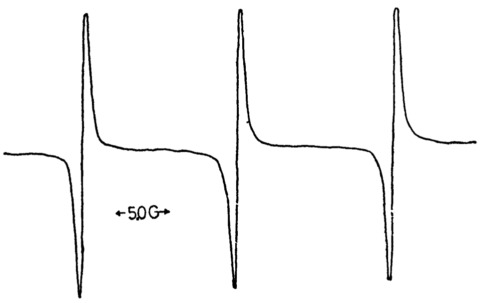


Fig. 2(d). The spectrum of an irradiated mixture of $p\text{-}\mathrm{MeC_6H_4SO_2I}$ and t-Bu-N=O in ether ($A_N = 12.5$ G).

by X. In contrast with the case of the photolysis of azosulfone Ia in the presence of X, phenyl radical was trapped by X in the photolysis of iodobenzene. In this case, iodobenzene was used in a high concentration, and therefore not all of the phenyl radicals produced were consumed by the reaction with ether.

Thus, the spin trapping experiments with nitrones II, III and 2-methyl-2-nitrosopropane (X) have proved that aryl radicals and sulfonyl radicals are produced by the thermolysis or photolysis of azosulfones Ia or Ib.

Experimental

Materials. Arylazo *p*-tolyl sulfones were synthesized by the addition of aqueous solutions of *p*-toluenesulfinate to aqueous solutions of arenediazonium salts,[4] and recrystallized from methanol. Nitrone II was produced by the condensation of phenylhydroxylamine with benzaldehyde, and recrystallized from ethanol. Nitrone III was synthesized by the following two steps; 1) $H_2O_2(90\%)$-Ac_2O-oxidation of benzylidene-*t*-butylamine to 2-*t*-butyl-3-phenyloxaziridine and 2) isomerization of the oxaziridine by refluxing in acetonitrile for 2 days.[16] It was recrystallized from hexane; mp 76 °C.

ESR Measurements. ESR signals were observed by use of a JES-ME-1X.

Formation of Benzhydryl Phenyl Nitroxide Radical IVa. Benzhydryl bromide, phenylhydroxylamine and sodium acetate were ground in a porcelain mortar. When the mixture was washed with water and then with hexane and the residue was recrystallized from benzene-hexane, *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was obtained. This hydroxylamine was also synthesized from α,*N*-diphenyl nitrone II and phenylmagnesium bromide.

Oxidation of VIa with HgO or 2,6-dichlorophenol-indophenol sodium was attempted, but was not successful. However, when air was bubbled through a weakly alkaline (NaOH) aqueous ethanol solution of VIa, ESR signals were observed. The same ESR signals were observed when a benzene solution of VIa containing some *n*-butyl lithium was irradiated with a high pressure mercury lamp. The hyperfine splittings of the ESR signals were identical with those obtained from azosulfone Ia and nitrone II, and are ascribable to benzhydryl phenyl nitroxide radical IVa.

Formation of t-*Butyl Phenyl*-p-*methoxyphenylmethyl Nitroxide Radical IVb.* *N*-*t*-Butyl-*N*-(phenyl-*p*-methoxyphenylmethyl) hydroxylamine (VIb) was prepared from α-phenyl *N*-*t*-butyl nitrone and *p*-methoxyphenylmagnesium bromide, and was oxidized by air in a weakly alkaline (NaOH) aqueous ethanol solution. The ESR signals observed were identical with those obtained in the reaction between azosulfone Ib and nitrone III, and are ascribable to *t*-butyl phenyl-*p*-methoxyphenylmethyl nitroxide radical IVb.

Products of the Reaction between Azosulfone Ia and Nitrone II. A mixture of Ia (2.5 g), II(4.0 g), pyridine (4.0 g) and benzene (130 ml) was heated at 91 °C for 3 hr (the half-life of Ia under these conditions is 46 min). The reaction mixture was washed with water and with dilute HCl for removal of pyridine, and then concentrated. The column chromatography (Florisil) of the residue gave biphenyl 10.8, azobenzene 6.1, *o*-benzhydrylaminophenyl *p*-toluenesulfonate (VIII) 17.2 and *p*-benzhydrylaminophenyl *p*-toluenesulfonate (IX) 1.0 mol/100 mol Ia.

Synthesis of VIII. *o*-Nitrophenyl *p*-toluenesulfonate was reduced with $SnCl_2$-HCl, and the *o*-aminophenyl *p*-toluenesulfonate obtained (1.5 g) was heated with benzhydryl chloride (1.0 g) and pyridine (5 ml) at 90 °C for 3 days. The reaction mixture was washed with water and then with dilute HCl, and pyridine was distilled off under reduced pressure. Recrystallization of the residue from hexane-benzene gave VIII; mp 122—123 °C.

Synthesis of IX. A mixture of *p*-aminophenyl *p*-toluenesulfonate (1.5 g), benzhydryl chloride (1.0 g) and pyridine (5 ml) was refluxed for 13 hr and then treated in a manner similar to that described for VIII. Recrystallization from hexane-benzene gave IX; mp 133—134 °C.

Analysis:	C	H	N	M.W.
VIII (authentic)	72.38	5.37	3.13%	
VIII (from Ia and II)	72.87	5.43	3.09	419
IX (authentic)	71.21	5.31	2.99	
IX (from Ia and II)	69.85	5.31	3.41	421
Calcd.	72.8	5.4	3.3	429

Molecular weights were determined by use of the vapor pressure method with a Hitachi-Perkin Elmer Molecular Weight Apparatus 115.

Footnotes

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