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Spin Trapping of Aryl and Arylcyclohexadienyl Radicals by *N*-*t*-Butyl-*α*-phenylnitrone (*N*-Benzylidene-*t*-butylamine Oxide) and *α*,*N*-Diphenylnitrone (*N*-Benzylideneaniline Oxide)[1]

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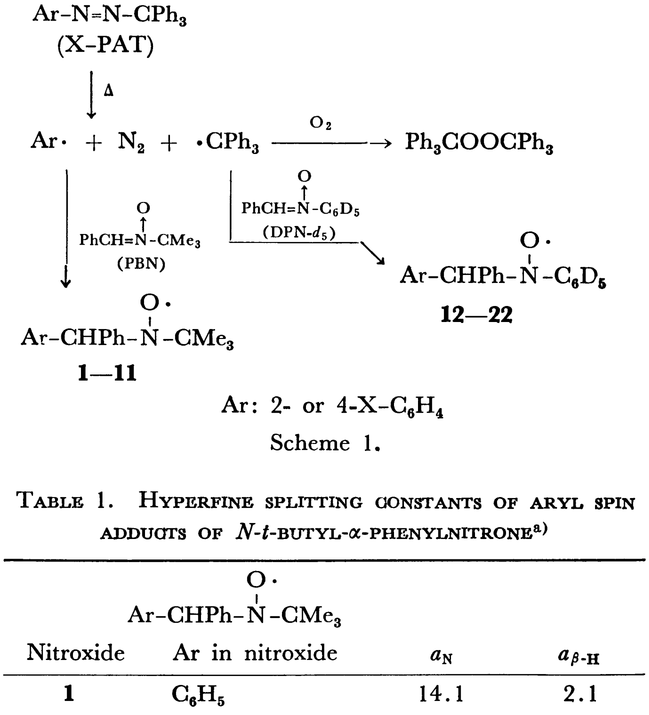
Monosubstituted phenyl radicals produce only aryl spin adducts in the reaction with nitrones described in the title, while polyhalo-substituted phenyl radicals add to solvent benzene, in competition with the formation of aryl spin adducts, to give arylcyclohexadienyl radicals, which in turn are trapped by the nitrones giving nitroxides incorporating the solvent benzene (Scheme 3).

The relative merits and applications of spin traps have been well discussed. Of various spin traps, comparison of the scavenging ability to some limited radicals was made.[2] For example, nitrones are shown to offer considerable advantages over nitroso compounds as a probe for alkoxyl radicals.[3] However, little is known about the relative reactivity of different radicals to a given spin trap. Previously we reported the decomposition of arylazotriphenylmethanes in benzene in the presence of nitrosodurene (2,3,5,6-tetramethylnitrosobenzene)[1] and showed that the aryl radicals carrying electron donating groups add to nitrosodurene to give aryldurylnitroxides (*N*-aryl-2,3,5,6-tetramethylanilinyloxyls),[1] the aryl spin adducts, while those with electron withdrawing groups produce no such aryl spin adducts, but afford spin adducts incorporating the solvent benzene.[4] The relative reactivity of different aryl radicals to nitrosodurene and benzene changes according to the nature of substituents attached to the aryl radicals. We have undertaken a study on decomposition of arylazotriphenylmethanes in benzene in the presence of *N*-*t*-butyl-α-phenylnitrone (PBN) and *N*-pentadeuteriophenyl-α-phenylnitrone (DPN-d_5) in order to see whether aryl radicals behave in a similar manner to the nitrones or not, and the results are described in this paper.

Results and Discussion

Reaction of Monosubstituted Phenyl Radicals with Nitrones. The thermal decomposition of phenylazotriphenylmethane (PAT) at 80 °C in benzene or in carbon tetrachloride containing *N*-*t*-butyl-α-phenylnitrone (PBN) under an atmosphere of argon gave an ESR spectrum of a triphenylmethyl radical and a nitroxide (**1**; $a_N=14.1$ and $a_{\beta\text{-H}}=2.1$ G) with the same hyperfine splitting constants as obtained for the phenyl spin adduct.[5] However, the signals of the triphenylmethyl radicals disappeared on standing or on exposure to air, presumably due to the reaction with oxygen. Similarly, 2- or 4-substituted phenylazotriphenylmethanes (2- or 4-X–PAT) produced the corresponding aryl spin adducts of PBN in both benzene and carbon tetrachloride (Scheme 1). The structural assignment of the spin adducts is based on the consistency of the hfsc's within the series, which are recorded in Table 1.



Scheme 1.

Table 1. Hyperfine splitting constants of aryl spin adducts of *N*-*t*-butyl-α-phenylnitrone[a]

$\mathrm{Ar{-}CHPh{-}\overset{\displaystyle O\cdot}{N}{-}CMe_3}$

Nitroxide	Ar in nitroxide	a_N	$a_{\beta\text{-H}}$
1	C_6H_5	14.1	2.1
2	4-CH_3-C_6H_4	14.0	2.2
3	4-CH_3O-C_6H_4	14.0	2.1
4	4-Cl-C_6H_4	14.0	2.1
5	4-Br-C_6H_4	14.0	2.1
6	4-NO_2-C_6H_4	13.9	2.1
7	2-CH_3-C_6H_4	14.0	3.2
8	2-CH_3O-C_6H_4	14.0	2.7
9	2-CH_3S-C_6H_4	14.0	2.8
10	2-Cl-C_6H_4	14.0	2.9
11	2-Br-C_6H_4	14.0	3.1

a) In G in benzene and carbon tetrachloride at room temperature.

When α,*N*-diphenylnitrone was used as a spin trap in the decomposition of PAT, an ESR spectrum consisting of complex sets identified as the phenyl spin adduct was observed.[6] By the use of *N*-pentadeuteriophenyl-α-phenylnitrone (DPN-d_5) as a spin trap the spectrum of the phenyl spin adduct was simplified to a signal composed of broad three doublets (**12**; $a_N=10.4$ and $a_{\beta\text{-H}}=3.4$ G) (Fig. 1). Similar spectra were obtained in the decomposition of 2- and 4-X–PAT's in

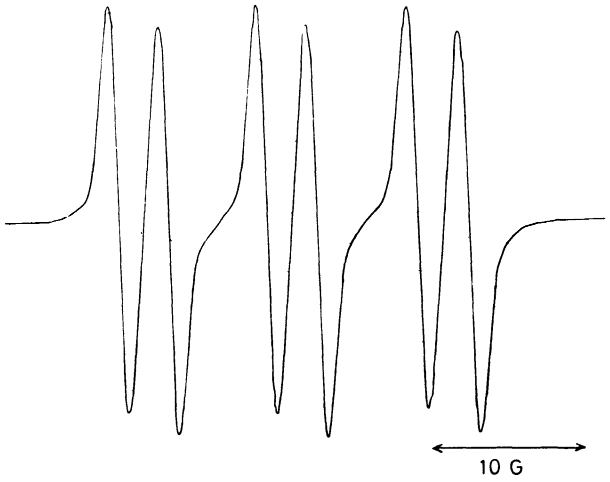


Fig. 1. The ESR spectrum of **12** obtained from the decomposition of PAT in benzene at 80 °C in the presence of DPN-d_5.

TABLE 2. HYPERFINE SPLITTING CONSTANTS OF ARYL SPIN ADDUCTS OF *N*-PENTADEUTERIOPHENYL-α-PHENYLNITRONE[a)]

$Ar\text{-}CHPh\text{-}\overset{O\cdot}{N}\text{-}C_6D_5$

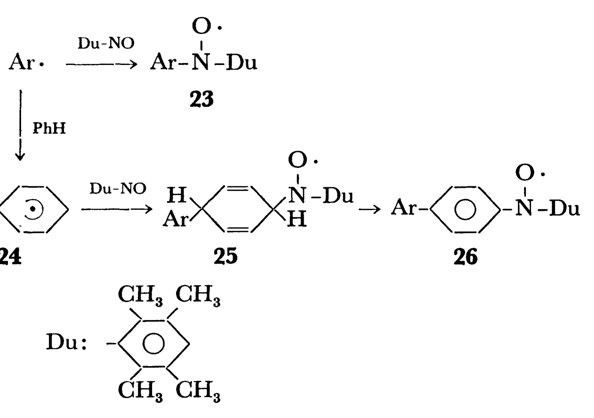
Nitroxide	Ar in nitroxide	a_N	$a_{\beta\text{-H}}$
12	C_6H_5	10.4	3.4
13	$4\text{-}CH_3\text{-}C_6H_4$	10.1	3.5
14	$4\text{-}CH_3O\text{-}C_6H_4$	10.2	3.6
15	$4\text{-}Cl\text{-}C_6H_4$	10.2	3.4
16	$4\text{-}Br\text{-}C_6H_4$	10.2	3.4
17	$4\text{-}NO_2\text{-}C_6H_4$	10.2	3.4
18	$2\text{-}CH_3\text{-}C_6H_4$	10.1	4.5
19	$2\text{-}CH_3O\text{-}C_6H_4$	10.2	3.8
20	$2\text{-}CH_3S\text{-}C_6H_4$	10.1	4.2
21	$2\text{-}Cl\text{-}C_6H_4$	10.2	4.0
22	$2\text{-}Br\text{-}C_6H_4$	10.2	4.1

a) In G in benzene and carbon tetrachloride at room temperature.

both benzene and carbon tetrachloride and the ESR parameters are shown in Table 2.

We showed previously[4)] that the aryl radicals having an electron donating substituent, such as methyl and methoxy at the 4 position, are trapped directly by nitrosodurene (Du–NO) in benzene to produce the aryl spin adducts (**23**). On the contrary, the aryl radicals with an electron withdrawing group, like chloro, bromo, or nitro group, add exclusively to benzene to give arylcyclohexadienyl radicals (**24**), which are subsequently trapped by Du–NO to yield the nitroxides (**25** and **26**) incorporating the solvent benzene (Scheme 2). However, this is not the case for the nitrones, PBN and DPN-d_5. The aryl radicals carrying a substituent at the *ortho* or the *para* position produced only the aryl spin adducts of PBN (**1**—**11**) and DPN-d_5 (**12**—**22**).

Substituent effects on the ESR spectra of various nitroxides have been reported and the nitrogen hfsc's in nitroxides are known to be correlated with the Hammett σ constants.[7)] To illustrate this relationship furthermore, the N hfsc's of the 4-substituted phenyldurylnitroxides[4)] (**23**) are plotted against σ. The correlation is only approximate, but the ρ value ($\rho=-1.2$, correlation coefficient=0.93) is consistent with the value reported for 4-substituted anilinyloxyl (Ar–NHO·; $\rho=-1.2$).[8)]



Scheme 2.

In the aryl spin adducts of PBN (**1**—**11**) and DPN-d_5 (**12**—**22**), the substituents attached to the β-phenyl group might exert influence on the N hfsc's. The data listed in Tables 1 and 2, however, show that the N hfsc's are essentially the same irrespective of the substituents within each series (**1**—**11** and **12**—**22**). The β-aryl group is two bonds apart from the nitrogen atom in both species of the nitroxides (**1**—**22**) and thus, the effect of substituents does not extend as far as the nitrogen atom through the bonds.

Other features emerged from the data are that the β-H hfsc does not depend on the nature of the substituents, but on the position of the substituents in the respective nitroxides. The nitroxides having the *ortho*-substituents (**7**—**11** and **18**—**22**) and those with the *para*-ones (**2**—**6** and **13**—**17**) are distinguished definitely to different groups. Thus, operation of other factors such as steric effect is suspected and this problem will be further discussed in the latter part.

Reaction of Polysubstituted Phenyl Radicals with Nitrones. The decomposition of 2,4,6-tribromophenylazotriphenylmethane (Br_3–PAT) in carbon tetrachloride containing PBN (30 mM) at 80 °C gave a spectrum ascribable to a 2,4,6-tribromophenyl spin adduct (**28**; $a_N=14.0$ and $a_{\beta\text{-H}}=7.5$ G) (Fig. 2-A), while in benzene Br_3–PAT produced another nitroxide (**33**; $a_N=14.1$ and $a_{\beta\text{-H}}=2.1$ G) along with **28** and triphenylmethyl radicals (Fig. 2-B). Since **33** is only produced in benzene, the incorporation of the solvent benzene in **33** is inferred. The relative intensity of **28** to **33** in the ESR spectra was raised with increasing amounts of PBN (see Figs. 2-C and 2-D). These facts indicate that **28** is formed directly by the reaction of 2,4,6-tribromophenyl radicals with PBN, while **33** is not. From the analogy of the reaction of aryl radicals with Du–NO, it is suggested that 2,4,6-tribromophenyl radicals add benzene to form arylcyclohexadienyl radicals (**24**; Ar=$2,4,6\text{-}Br_3C_6H_2$) in competition to the reaction with PBN. The intermediate radicals (**24**) are further scavenged by PBN to give the spin adduct (**33**). Since triphenylmethyl radicals are observed in the spectra, the further

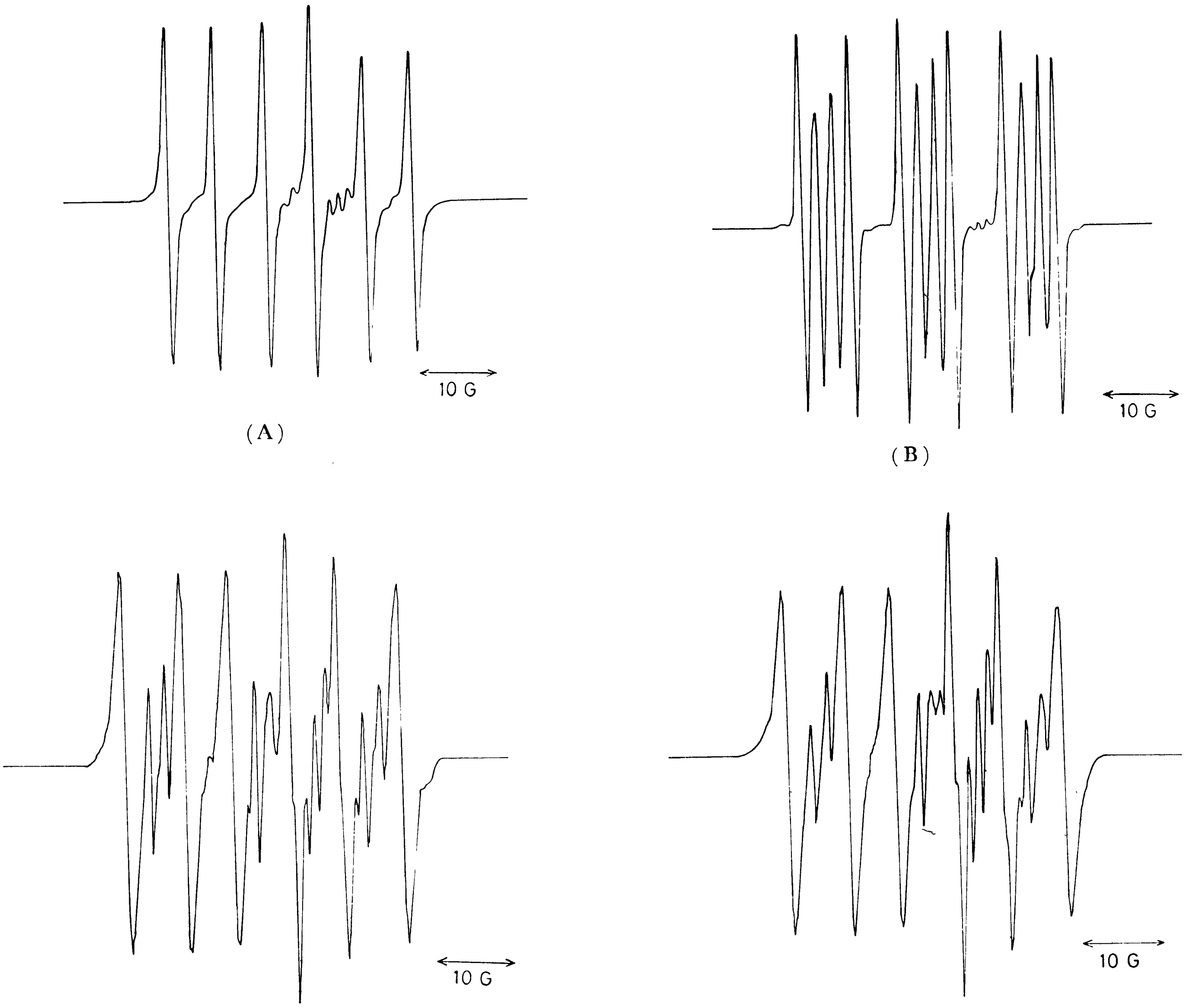
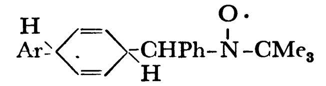
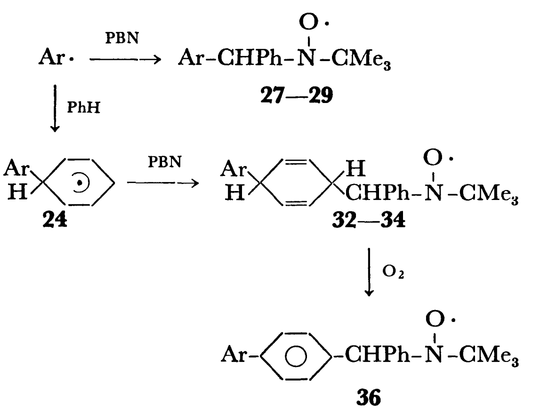


Fig. 2. (A) The ESR spectrum of **28** obtained from the decomposition of Br_3-PAT in carbon tetrachloride at 80 °C in the presence of PBN (30 mM). (B) The ESR spectrum obtained from the decomposition of Br_3-PAT in benzene at 80 °C in the presence of PBN (30 mM). The spectrum is due to both **28** and **33**. (C) The ESR spectrum of **28** and **33** obtained from the decomposition of Br_3-PAT in benzene at 80 °C in the presence of PBN (68 mM). (D) The ESR spectrum of **28** and **33** obtained from the decomposition of Br_3-PAT in benzene at 80 °C in the presence of PBN (135 mM). A small concentration of triphenylmethyl radicals is always present in all the cases.

Table 3. HYPERFINE SPLITTING CONSTANTS OF NITROXIDES OBTAINED IN THE DECOMPOSITION OF POLYSUBSTITUTED PHENYLAZOTRIPHENYLMETHANES (X_n-PAT) IN BENZENE CONTAINING PBN

X_n-PAT	Aryl radicals generated (Ar·)	Nitroxides[a)]					
		Ar-CHPh-N(O·)-CMe_3[b)]					
			a_N	$a_{\beta\text{-H}}$		a_N	$a_{\beta\text{-H}}$
Cl_3-PAT	2,4,6-$Cl_3C_6H_2$·	**27**	13.9	6.6	**32**	14.0	2.1
Br_3-PAT	2,4,6-$Br_3C_6H_2$·	**28**	14.0	7.5	**33**	14.1	2.1
F_5-PAT	C_6F_5·	**29**	14.0	4.4	**34**	13.8	2.1
Me_3-PAT	2,4,6-$Me_3C_6H_2$·	**30**[c)]	14.5	8.8	**35**[d)]	14.0	2.2

a) In G in benzene at room temperature. b) Unless otherwise noted, the same spectrum was obtained in CCl_4. c) A trichloromethyl spin adduct (**31**; $a_N=13.6$, $a_{\beta\text{-H}}=1.6$ G) was obtained concurrently in CCl_4. d) The structure was tentatively assigned to a 3,5-dimethylbenzyl spin adduct (**35a**).



Ar: 2,4,6-$Cl_3C_6H_2$ (**27** and **32**), 2,4,6-$Br_3C_6H_2$ (**28** and **33**), and C_6F_5 (**29** and **34**).

Scheme 3.

oxidation of **33** to a nitroxide (**36**; Ar=2,4,6-$Br_3C_6H_2$) by molecular oxygen is highly improbable (Scheme 3).

Similar results were obtained with 2,4,6-trichloro-(Cl_3–PAT) and 2,3,4,5,6-pentafluoro-phenylazotriphenylmethane (F_5–PAT) in carbon tetrachloride and benzene. The hfsc's of the nitroxides obtained are recorded in Table 3.

Migita and his co-workers[9] reported recently that the relative rate of addition of 4-nitrophenyl radicals and phenyl radicals to benzene is 5.6 at 60 °C. Accordingly, electron withdrawing halogen substituents increase the rate of addition of the aryl radicals to benzene, but the effect is small. Thus, the formation of the benzene incorporated nitroxides (**32**—**34**) may be accounted for in view that the rate of addition of aryl radicals to PBN is much suppressed in the polyhalogenated phenyl radicals than in phenyl ones due to steric or electronic effects.

When 2,4,6-trimethylphenylazotriphenylmethane (Me_3–PAT) was decomposed in carbon tetrachloride in the presence of PBN, ESR spectra due to two nitroxides were observed (Fig. 3-A). One spectrum was attributed to a 2,4,6-trimethylphenyl spin adduct (**30**; $a_N=14.5$ and $a_{\beta\text{-H}}=8.8$ G) by analogy with the values obtained for the polyhalophenyl spin adducts (**27**—**29**). Further verification for the structural assignment of **30** was obtained in the decomposition of PAT with *N*-*t*-butyl-α-2,4,6-trimethylphenylnitrone [*N*-(2,4,6-trimethylbenzylidene)-*t*-butylamine oxide; Me_3–PBN] in benzene. The ESR spectrum obtained is completely the same as that observed above. The other spectrum was assigned as a trichloromethyl spin adduct (**31**; $a_N=13.6$ and $a_{\beta\text{-H}}=1.6$ G), because the same spectrum was independently produced from the photolysis of di-*t*-butyl peroxide in chloroform in the presence of PBN (Scheme 4). Chlorine abstraction from carbon tetrachloride by 2,4,6-trimethylphenyl radicals may be facilitated by the electron donating substituents on the phenyl radicals[10] to afford trichloromethyl radicals, which were subsequently trapped by PBN.

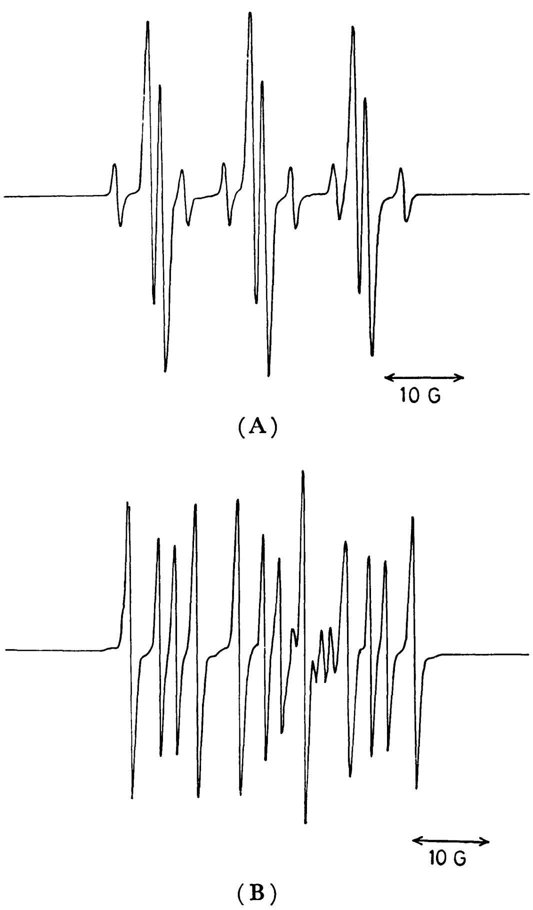
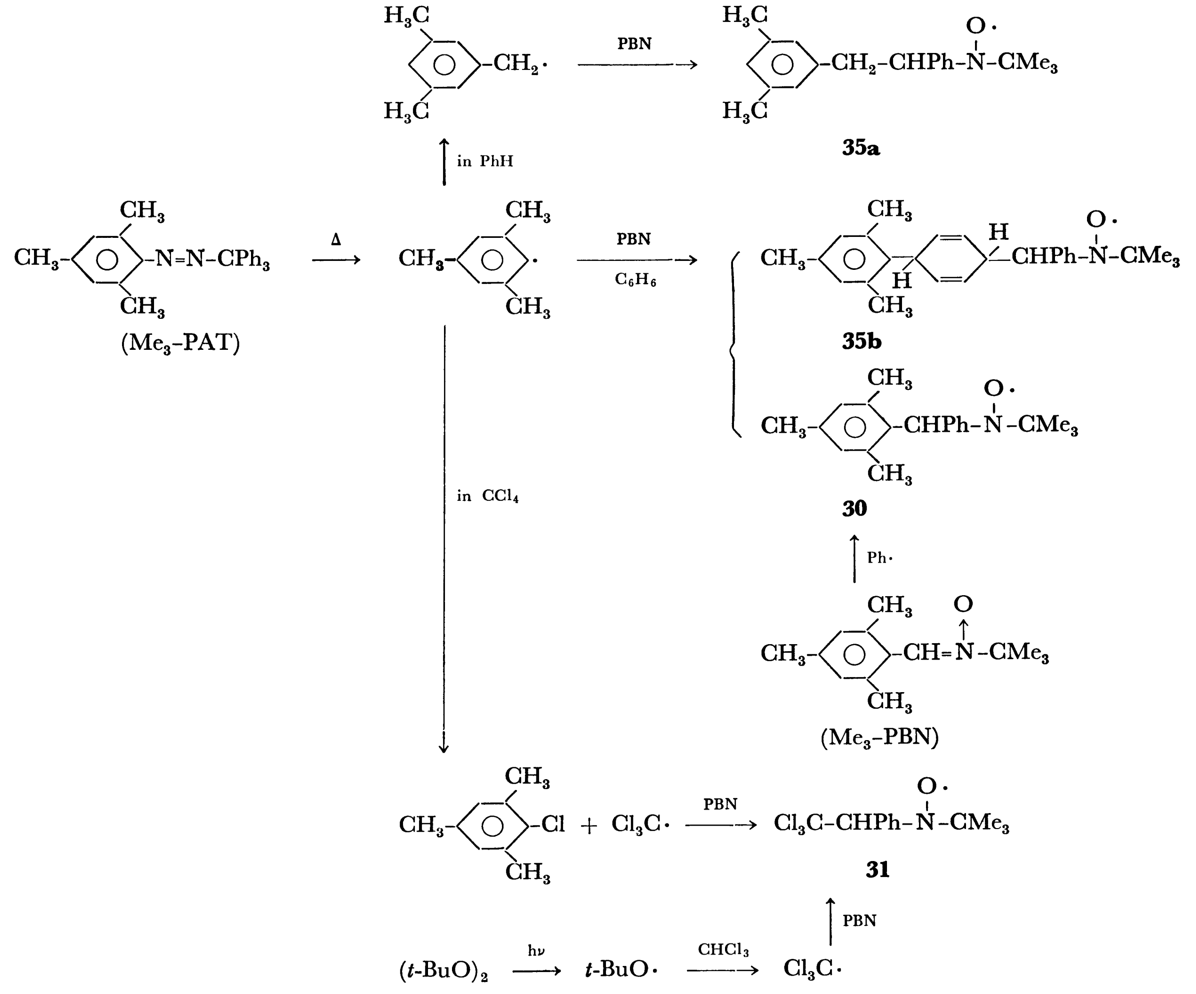


Fig. 3. (A) The ESR spectrum of **30** and **31** obtained from the decomposition of Me_3-PAT in carbon tetrachloride at 80 °C in the presence of PBN. (B) The ESR spectrum of **30** and **35a** obtained from the decomposition of Me_3-PAT in benzene at 80 °C in the presence of PBN. A small concentration of triphenylmethyl radicals is also present.

In benzene, Me_3–PAT produced another nitroxide as well as **30** with PBN (Fig. 3-B). The newly formed nitroxide (**35**; $a_N=14.0$ and $a_{\beta\text{-H}}=2.2$ G) has almost the same N and β-H hfsc's as those of **33**. Thus, incorporation of the solvent benzene in the nitroxide (**35**) was suspected. Recently, it was found by the use of CIDNP technique that the rearrangement of 2-methylphenyl radicals to benzyl radicals occurs during the thermolysis of bis(2-methylbenzoyl) peroxide.[11] If such a rearrangement would take place for the 2,4,6-trimethylphenyl radicals, the resulting 3,5-dimethylbenzyl radicals would produce a spin adduct (**35a**) consistent with the observed spectrum. Since a benzyl spin adduct is known to have similar hfsc's ($a_N=13.9$ and $a_{\beta\text{-H}}=2.4$ G)[5] to those of **35**, assignment of **35a** is also consistent with the observation. Thus, the structure of the nitroxide (**35**) could be assigned as either the 3,5-dimethylbenzyl spin adduct (**35a**) or 2,4,6-trimethylphenylcyclohexadienyl spin adduct (**35b**). Judging from the known behavior of aryl radicals to benzene,[9] the reactivity of 2,4,6-trimethylphenyl radicals is supposed to be lowered, and the formation of the benzene incorporated nitroxide **35b** is implausible. Accordingly, the nitroxide is believed to be **35a** rather than **35b**.

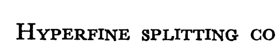
With Me_3–PBN, Cl_3–PAT produced a trichlorophenyl spin adduct (**37**; $a_N=14.1$ and $a_{\beta\text{-H}}=8.8$ G) in carbon tetrachloride. The same spectrum was obtained in benzene, but none of signals due to a benzene in-


Scheme 4.

corporated nitroxide were observed. These findings show that Me_3–PBN is much more efficient than PBN in trapping of 2,4,6-trichlorophenyl radicals. In other words, the 2,4,6-trichlorophenyl radical is electrophilic and the transition state has some polar character with electron donation from Me_3–PBN. The view is borne out, because the rate of addition of the electrophilic benzoxyl radical to PBN is known to increase with electronegative substituents on PBN (Hammett ρ against $\sigma^+ = -0.47$).[12]

The decomposition of Cl_3–PAT, Br_3–PAT, and F_5–PAT in CCl_4 in the presence of DPN-d_5 gave the corresponding aryl spin adducts (**38**—**40**) (Table 4).

TABLE 4. HYPERFINE SPLITTING CONSTANTS OF ARYL SPIN ADDUCTS OF DPN-d_5[a)]


$\text{Ar-CHPh-}\overset{\text{O}\cdot}{\text{N}}\text{-C}_6\text{D}_5$

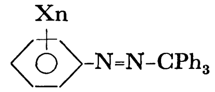
Nitroxide	Ar in nitroxide	a_N	$a_{\beta\text{-H}}$
38[b)]	2,4,6-$Cl_3C_6H_2$	9.8	6.5
39[b)]	2,4,6-$Br_3C_6H_2$	9.8	6.5
40	C_6F_5	10.2	5.6

a) In G in carbon tetrachloride at room temperature.
b) The same spectra were obtained in benzene.

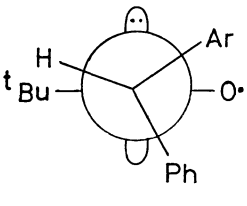
In benzene containing DPN-d_5, Cl_3–PAT produced **38** and another nitroxide (**41**), but the spectra observed are not well resolved. Br_3–PAT produced definitely a similar mixture of **39** and **42**, while F_5–PAT gave only a benzene incorporated nitroxide (**43**; $a_N = 10.3$ and $a_{\beta\text{-H}}' = 3.5$ G). The structure of **41** and **42** was believed to be the benzene incorporated nitroxides by the analogy with the behavior of polyhalogenated phenyl radicals to PBN.

Finally, it is of interest to discuss conformations of the nitroxides obtained. Since the $a_{\beta\text{-H}}$ value depends on the dihedral angle between the C–H bond and the p orbital on the nitrogen atom, the generally low $a_{\beta\text{-H}}$ values of the nitroxides listed in Tables 1 (**1**—**6**) and 2 (**12**—**17**) certainly indicate that the C–H bond lies close to the plane perpendicular to the p orbital on the nitrogen atom. The nitroxides should then be assigned as the *trans* conformer (**44**), in which the C–H bond is approximately *trans* with respect to the N–O bond, between two preferred conformers. The *cis* conformer should be disregarded because of large steric hindrance between the two aryl and *t*-butyl groups. Thus, we infer that, for the species with *ortho* substituents, the steric repulsion between the *ortho* group and the oxygen atom in the *trans* conformer (**44**) causes the twisting around the C–H bond, resulting in a decrease of the dihedral angle and in concomitant higher $a_{\beta\text{-H}}$ values (**45**).

Table 5. Substituted phenylazotriphenylmethanes (X_n-PAT's)

 Compd X_n in X_n-PAT	Mp (dec), °C	Elemental analysis, %						
		Found			Molecular formula	Calcd		
		C	H	N		C	H	N
2,4,6-Me_3	101—102	86.29	6.71	6.89	$C_{28}H_{26}N_2$	86.29	6.71	7.17
2,4,6-Br_3	125—126	51.23	2.92	4.87	$C_{25}H_{17}N_2Br_3$	51.30	2.90	4.79
2,4,6-Cl_3	116.5—117.0	66.61	4.15	6.35	$C_{25}H_{17}N_2Cl_3$	66.44	3.76	6.20
2,3,4,5,6-F_5[a]	81.5—82.0	69.92	3.85	6.42	$C_{25}H_{15}N_2F_5$	68.49	3.42	6.39
2-SMe	127—127.5	78.99	5.72	7.17	$C_{26}H_{22}N_2S$	79.15	5.62	7.10

a) In spite of careful and repeated purification on recrystallization from benzene-ethanol, the results of C-H analysis are not satisfactory. The inconsistency with the calculated values may be ascribed to its instability.



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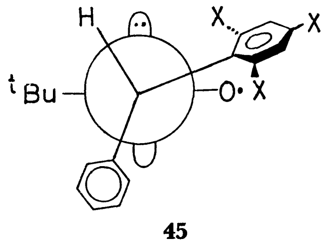

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Experimental

Materials. *N-t*-Butyl-α-phenylnitrone[13] (PBN) and substituted phenylazotriphenylmethanes[14,15,16] (X_n-PAT's) were prepared according to published procedures. Newly prepared X_n-PAT's were listed in Table 5.

N-*Pentadeuteriophenyl-α-phenylnitrone (DPN*-d$_5$*).* DPN-d_5 was obtained in a method similar to the preparation of α,*N*-diphenylnitrone:[17] mp 106—107 °C (from ethanol); NMR ($CDCl_3$) δ 2.0(s, 1H, vinyl proton) and 7.5—8.5(m, 5H, phenyl protons). Found: C, 77.07; H, 8.80; N, 6.92%. Calcd for $C_{13}H_6D_5NO$: C, 77.19; H, 7.97; N, 6.92%.

N-t-*Butyl-α-2,4,6-trimethylphenylnitrone (Me$_3$-PBN).* To a mixture of 2,4,6-trimethylbenzaldehyde (3.5 g) and *t*-butylamine (8.0 g) in 10 ml of benzene was added dropwise a solution of $TiCl_4$ (2.3 g) in 20 ml of benzene at 0 °C with stirring. After the addition was completed, the mixture was allowed to warm at room temperature and left for 3 days. The precipitate was filtered off and the filtrate was concentrated on evaporation of the solvent under reduced pressure. Residual oil (1.9 g) was oxidized and isomerized in similar ways described in the literature:[13] mp 112—114 °C (from hexane); NMR($CDCl_3$) δ 2.2(s, 1H, vinyl proton), 1.6(s, 9H, *t*-butyl protons), 2.2(s, 9H, methyl protons), and 6.9—7.7(m, 2H, aromatic protons). Found: C, 76.67; H, 9.81; N, 6.22%. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39%.

Thermal Decomposition of Arylazotriphenylmethanes. A solution of arylazotriphenylmethanes (10 mM) in benzene or carbon tetrachloride containing *N-t*-butyl-α-phenylnitrone or *N*-pentadeutetriophenyl-α-phenylnitrone (30 mM) was purged with argon for 2 min in an ESR tube in order to remove dissolved oxygen, and was heated at 80 °C for 3 min. ESR signals were observed by use of a JEOL JES-ME-1X spectrometer.

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1) In the present paper trivial names such as nitrones and nitroxides are used instead of systematic names, because these terms have found wide use in literatures. The systematic names are shown in parentheses.

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