and to complete decomposition of the cyclic sulfone, respectively, were collected in a liquid air trap and purified on a vacuum line, and the ${}^{32}S/{}^{34}S$ mass ratios were determined as previously described.³⁰

Nmr spectra were recorded on a Varian A-60A instrument.

Registry No.-I, 77-79-2; II, 20966-34-1; III,

(30) W. H. Saunders, Jr., and S. Ašperger, J. Amer. Chem. Soc., 79, 1612 (1957).

10033-92-8; IV, 34206-55-8; deuterium, 7440-51-9; sulfur-34 isotope, 13965-97-4.

Acknowledgment.—The authors thank Professor Maurice Kreevoy and Professor Elliot N. Marvell for most helpful discussions. Thanks are due to Dr. J. Popović for help in measuring mass spectra.

α-Phenylnitroxide Radicals from α-Phenylnitrones¹

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Irradiation of α -phenyl-*N*-tert-butylnitrone in benzene in the presence of some organometallic reagents traps short-lived radicals. The nitroxide radical formed is dependent on the amount of oxygen in solution. The inherent quality of α ,*N*-diphenylnitrone to lose oxygen on irradiation allows only one of the above type nitroxide radicals. Nitroxide radicals are also formed when the phenylnitrones are irradiated in benzene containing alcohols. This reaction apparently does not proceed via the usual trapping mode. The reactions and structures of the nitroxides are discussed.

In a recent study we reported that α -phenylnitrones² on irradiation with ultraviolet light gave rise to Nbenzoylnitroxide radicals.³ The spin trapping characteristic of α -phenyl-N-tert-butylnitrone (PBN) has been dealt with in a number of papers.⁴ In the spin trapping technique, a reactive free radical adds to PBN to produce a stabler nitroxide radical. The hyperfine splitting constants (hfsc's), from esr measurements, of the α -hydrogen and nitrogen atoms show slight variations with different trapped radicals, R. This paper describes additional radicals arising from nitrones that we have detected under various conditions.

Results

Nitroxide Radicals from α -Phenyl-N-tert-butylnitrone.—When we irradiated, with ultraviolet light, benzene solutions of PBN to which organolead and -mercury compounds had been added, the esr signal obtained depended on the degree of deoxygenation of the solution. Incompletely deaerated solutions of PBN in benzene containing dimethylmercury, diethylmercury, triethyllead acetate, tetra-n-butyllead, or diphenylmercury yielded radicals whose hfsc's differed from those reported by Janzen and Blackburn,^{5,6} but still showed

(1) Presented in part at the 9th National Meeting of the Society for Applied Spectroscopy, New Orleans, La., Oct 1970.

(2) In this paper the carbon substituents X and Y are prefixed by α , and the substituent on the nitrogen (R) is prefixed by N.



Hyperfine splitting constants from esr measurements referring to the hydrogen on the carbon atom are designated as A_a^{H} .

(3) A. L. Bluhm and J. Weinstein, J. Amer. Chem. Soc., 92, 1444 (1970).
 (4) See E. G. Jantzen, Accounts Chem. Res., 4, 31 (1971), for a review of

spin trapping including the nitrones and references thereto.

(5) E. G. Janzen and B. J. Blackburn, J. Amer. Chem. Soc., 90, 5909 (1968).

(6) E. G. Janzen and B. J. Blackburn, ibid., 91, 4481 (1969).

the typical splitting pattern, a triplet of doublets, arising from a sharing of the odd electron between the nitrogen and α -hydrogen atoms. When fresh solutions were completely deaerated and then irradiated, the splitting constants agreed with the values reported. The splitting constants are listed in Table I. In the

TABLE I Hyperfine Splitting Constants of Nitroxides from α-Phenyl-N-tert-butylnitrone^a

Radical source	$A^{N \ b}$	$A \alpha^{\mathrm{H} b}$	A^{N} °	$A \alpha^{\mathrm{H}}$ °	$A^{N \ d}$	$A \alpha^{\mathrm{H}}$
$(CH_3)_2Hg$	13.74	1.99	14.79	3.73	14.82	3.60
$(CH_3CH_2)_2Hg$	13.80	1.97	14.68	3.25	14.62	3.33
(CH ₃ CH ₂) ₃ PbOAc	13.75	1.95	14.54	3.30	14.50	3,35
$n-\mathbf{Bu}_4\mathbf{Pb}$	13.65	1.97	14.64	3.21	14.62	3.27
$(C_6H_5)_2Hg$	13.65	1.97	14.47	2.18	14.42	2.21
$(C_6H_5)_3CN = NC_6H_5^e$			14.48	2.17^{e}	14.43	2.18

^a In benzene at room temperature. The splittings are in gauss. ^b Photolysis of incompletely deoxygenated solutions of PBN and radical source. ^c Photolysis of totally deoxygenated solutions of PBN and radical source. ^d Values from Janzen and Blackburn adjusted upwards by 4.4%.⁶ ^e By thermal decomposition.

deoxygenated solutions, the radical which attached to the nitrone system was either a methyl, ethyl, n-butyl, or phenyl radical, depending on the radical source.^{5,6} The hydrogen and nitrogen coupling constants which arose from incompletely deoxygenated solutions showed very little variation in value, which may indicate that a similar type of reactive species added to the nitrone function. We also observed that, when the totally deoxygenated solutions were irradiated briefly, for about 15 sec, the radicals detected were the ones with smaller hfsc's, shown in Table I. These signals were stable if the solutions were kept in the dark. On further irradiation, about 1-3 min, the nitroxide radicals with larger splitting constants were found. In partially deoxygenated solutions, the nitroxide with larger splitting constants was never observed, even after extended irradiation. Figure 1 shows the changes in the esr spectra during progressive stages of irradiation of a deoxygenated benzene solution of PBN containing diethylmercury. Figure 1b shows the esr signal as a mixture

TABLE II						
Comparison of Hyperfine Splitting Constants of Nitroxides by						
IRRADIATION OF PBN IN BENZENE WITH ADDITIVES ^a						

Additive	A^{N}	$A \alpha^{\rm H}$	α-Carbon substituent on nitroxide radical	Registry no.
$(CH_3)_2Hg^b$	14.79	3.73	CH_3	21894 - 27 - 9
$(CH_3)_2Hg^{\circ}$	13.74	1.99	OX.	
$CH_{3}OH + Pb(OAe)_{4}$	13.76	2.00	OCH_3	34234-86-1
$CH_3OH + H_2O_2$	13.87	3.82	$CH_{2}OH$	34280-33-6
$(CH_3CH_2)_2Hg^b$	14.68	3.25	$\rm CH_2 CH_3$	21894-28-0
$(CH_3CH_2)_2Hg^c$	13.80	1.97	OX.	
CH ₃ CH ₂ OH	14.08	2.05	OCH_2CH_3	34280 - 35 - 8
$CH_3CH_2OH + Pb(OAc)_4^d$	14,01	2.03	OCH_2CH_3	
$CH_3CH_2OH + H_2O_2$	14.07	3.12	CH(CH ₃)OH	34234 - 87 - 2
$n-\mathrm{Bu}_4\mathrm{Pb}^b$	14.64	3.21	<i>n</i> -Bu	21999 - 41 - 7
<i>n</i> -Bu₄Pb ^c	13.65	1.97	OX.	
n-BuOH	13.75	2.10	O-n Bu	34234 - 89 - 4
n-BuOH + Pb(OAc) ₄ ^d	13.82	2.00	O-n-Bu	
n-BuOH + H ₂ O ₂	14.17	3.09	$CH(CH_2CH_2CH_3)OH$	34234-90-7
tert-BuOH	13.74	2.10	O-tert-Bu	34234-91-8
tert-BuOH + Pb(OAc) ₄	13.79	2.01	O-tert-Bu	
tert-BuOH + H ₂ O ₂	14.04	3.23	$(CH_2)(CH_3)_2COH$	34234-92-9
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^a In gauss at room temperature. ^b Completely deoxygenated. ^c Partially deoxygenated. ^d No irradiation necessary. ^e See Discussion.

of two radicals at an intermediate point of irradiation. Irradiation of the nitrone in the presence of 1',1',1'triphenylbenzeneazomethane, a phenyl radical generator, yielded only one nitroxide radical independent of the degree of deoxygenation. Although we previously reported that irradiation of PBN in benzene yielded the N-benzoylnitroxide radical,³ it was not prominent in the signals from solutions containing the reactive additives.

The value of the coupling constants from partially deaerated solutions of PBN and the above organometallics were found to be of the same order as found for PBN and scavenged alkoxyl radicals, as shown further on. When solutions of PBN in benzene to which 1%of an alcohol was added were irradiated, we observed splittings also of the same order as those from scavenged alkoxyl radicals. The alcohol concentration could be increased and the signal would still be observed, but in 100% alcohol no signal was observed. The alcoholgenerated radical signals appeared very slowly on irradiation and were usually not strong. The higher instrumental modulation amplitudes used gave rise to broader signals. We examined benzene solutions of PBN in the presence of ethanol, ethanol and lead tetraacetate, and ethanol and hydrogen peroxide; and similar sequences with *n*-butyl alcohol and *tert*-butyl alcohol. The hfsc's are shown in Table II. From the solutions containing alcohols and lead tetraacetate, very strong signals appeared immediately. Forshult, Lagercrantz, and Torssell⁷ used 2-methyl-2-nitrosobutanone-3 as a scavenger for alkoxyl radicals developed in the reaction of alcohols and lead tetraacetate. With PBN



as a radical trap we would expect an analogous reaction. The hfsc's for PBN with alcohol present and with alcohol plus lead tetraacetate are identical, and this has led

(7) S. Forshult, C. Lagercrantz, and K. Torssell, Acta Chem. Scand., 23, 522 (1969).



Figure 1.— α -Phenyl-*N*-tert-butylnitrone in benzene plus diethylmercury. Solution deoxygenated by argon flushing for 30 min: (a) after 30 sec irradiation with unfiltered high-pressure mercury lamp; (b) after 1.5 min irradiation; (c) after 2 min irradiation.

us to believe that irradiation of nitrones in the presence of alcohols leads to the same nitroxide in which an alkoxyl group is attached at the α carbon. Additional evidence is given in this paper in the reaction of other nitrones and alcohols. Irradiation of a benzene solution of PBN containing only lead tetraacetate gave a weak esr signal with splittings about $A^{\rm N}$ 13.3 and $A_{\alpha}^{\rm H}$ 1.9 G, which may be attributed to trapping of acetoxy radical.⁶

Hydroxyalkyl radical species have been generated and trapped by irradiation of solutions of alcohol, hydrogen peroxide, and 2-methyl-2-nitrosobutanone-3.⁷ Utilizing this technique, we irradiated benzene solutions of PBN to which were added an alcohol and hydrogen

$$H_2O_2 \xrightarrow{h\nu} 2HO$$



peroxide. The splitting constants obtained differed from the other nitroxide radicals in which R and RO were attached to the α -carbon position. These values for methanol, ethanol, and *n*-butyl and *tert*-butyl alcohols are also shown in Table II. The nitroxide radical arising from *tert*-butyl alcohol and hydrogen peroxide with PBN gave splitting constant values which differed from those obtained by trapping of the *tert*-butyr radical generated in the presence of lead tetraacetate (Table II).

Nitroxide Radicals from α , N-Diphenylnitrone. $-\alpha$, N-Diphenylnitrone (DPN) when employed as a radical scavenger gives more complex esr spectra due to the sharing of the odd electron with the N-phenyl protons. However, in most of our experiments, the signals were clean and well resolved, leading to good interpretations.

Although DPN would be expected to behave similarly to PBN, we noted some differences during our studies. For example, on irradiation of the nitrones in benzene without additives, the signal of the benzoyloxy radical from DPN developed rapidly and in good strength. In contrast, the photoxidation radical from PBN showed more sluggish development.³ When solutions of DPN in benzene were irradiated in the presence of organomercury or -lead compounds, the signal observed was not dependent on the degree of deoxygenation, and was attributed to the trapping of either an alkoxyl or an alkylmetaloxyl group at the α position. The splitting constants, and those from thermal decomposition of 1',1',1'-triphenylbenzeneazomethane in DPN-benzene, are listed in Table III. The hfsc's for

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Hyperfine Splitting Constants of Nitroxides from α-Phenyl-N-phenylnitrone^α

		A ^{H b}			
Radical source	$A^{\mathbf{N}}$	Ortho, para	Meta	α	
$(CH_3)_2Hg$	10.57	2.49	0.90	1.60	
$(CH_3CH_2)_2Hg$	10.60	2.57	0.86	1.64	
(CH ₃ CH ₂) ₃ PbOAc	10.65	2.56	0.85	1.64	
<i>n</i> -Bu₄Pb	10.52	2.50	0.85	1.62	
$(C_6H_5)_3CN = NC_6H_5$	10.62	2.64	0.90	3.57	

^a In benzene at room temperature. The splittings are in gauss. ^b Ortho, para, and meta H's from N-phenyl group.

nitrogen and ortho, para, and meta hydrogen atoms were of the same order of magnitude for the different additives. The α -hydrogen value, however, was much larger when the additive was a phenyl radical precursor, in which case it is proposed that the species trapped was the phenyl group. The α -hydrogen splittings observed with the organometallic additives were duplicated by irradiating DPN in benzene containing various alcohols and were attributed to a nitroxide with XO attached to the α -carbon atom. The nature of the XO group is discussed further on. In general, the α -hydrogen splittings for XO groups attached at the α -carbon position were about 1.6 G and for R about 3.6 G. This generalization is reinforced by the following work.

In the presence of alcohols containing lead tetraacetate, benzene solutions of DPN, without irradiation, yielded the same coupling constants as observed in DPN-benzene solution irradiated with only alcohols present. The coupling constants are shown in Table IV. We also observed that the hfsc's of the nitroxide arising from irradiation of the nitrone in benzene with *tert*-butyl hydroperoxide present were identical with those obtained with the nitrone in the presence of *tert*butyl alcohol and *tert*-butyl alcohol plus lead tetraacetate. *tert*-Butyl hydroperoxide decomposes to give *tert*-butoxy and hydroxy radicals.

 α -Alkyl substituted nitroxides, which we were unable to prepare by the reaction of DPN and organolead or -mercury compounds, as they could be with PBN, were obtained by two different procedures. The irradiation of organic carboxylic acids in the presence of lead tetraacetate proceeds through a radical process⁸ according to the equation

$$\text{RCOOH} \xrightarrow{\text{Pb(OAc)}_4} \text{R} \cdot + \text{CO}_2$$

By this technique Forshult, Lagercrantz, and Torssell trapped alkyl radicals using nitroso compounds as scavengers.⁷ When we irradiated a benzene solution of DPN to which was added acetic acid and lead tetra-acetate, we obtained an esr signal with splittings $A^{\rm N}$ 10.67, $A_{\rm o,p}^{\rm H}$ 2.63 (3 H), $A_{\rm m}^{\rm H}$ 0.93 (2 H), and $A_{\alpha}^{\rm H}$ 3.60 G (1 H). This signal arises from the nitroxide radical with the methyl group joined to the α -carbon atom.

$$CH_{3}COOH \xrightarrow{Pb(OAc)_{4}} CH_{3} \xrightarrow{DPN} \begin{array}{c} H & O \\ I & I \\ C \\ C \\ CH_{3} \end{array}$$

The experimental esr spectra and simulated stick patterns are shown in Figure 2 for the nitroxide radicals with α -methyl and α -methoxyl substituents. In another experiment, *n*-butyllithium was added to the benzene solution of DPN, followed by air oxidation.

$$n \cdot \text{BuLi} + \text{DPN} \rightarrow$$

$$H \quad \text{OLi} \quad 0_{1} \qquad H \quad 0 \cdot \text{I} \quad 1 \quad 0_{1} \quad 0_{2} \quad 0_{2} \quad 0_{1} \quad 0_{1} \quad 0_{2} \quad 0_{$$

This technique was used by Janzen and Blackburn to form α -alkyl substituted nitroxides from PBN and organolithium or Grignard reagents.^{5,6} Previous reports demonstrated that Grignard reagents added to aldonitrones in a 1,3 manner.⁹ The coupling constants from butyllithium and DPN were $A^{\rm N}$ 10.71, $A_{\circ,p}^{\rm H}$ 2.71 (3 H), $A_{\rm m}^{\rm H}$ 0.90 (2 H), and $A_{\alpha}^{\rm H}$ 3.99 G (1 H). With phenyllithium we obtained $A^{\rm N}$ 10.61, $A_{\circ,p}^{\rm H}$ 2.68 (3 H), $A_{\rm m}^{\rm H}$ 0.90 (2 H), and $A_{\alpha}^{\rm H}$ 3.59 G (1 H), which are the same values as obtained by the trapping of

⁽⁸⁾ R. Criegee in K. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, Chapter 5.
(9) A. Angeli, L. Alessandri, and M. Aizza-Mancini, Atti Accad. Naz.

⁽⁹⁾ A. Angeli, L. Alessandri, and M. Aizza-Mancini, Atti Accad. Naz. Lincei, 20, 546 (1910); Chem. Abstr., 5, 3403 (1911); G. E. Utzinger and F. A. Regenass, Helv. Chim. Acta, 37, 1892 (1954).

TABLE	IV	
L A B L L		

Hyperfine Splitting Constants of Nitroxides from a-Phenyl-N-phenylautrone with Additives^a

			A ^{II b}		a-Carbon	Registry
Additive	A^{N}	Ortho, para	meta	α	substituent	no.
CH₃OH	10.74	2.58	0.97	1,62	OCH_{0}	34234-93-0
$CH_{3}OH + Pb(OAc)_{4}$	10.57	2.56	0.91	1.55	OCH_3	
$CH_{3}CH_{2}OH$	10.63	2.57	0.85	1.61	OCH_2CH_3	34234 - 94 - 1
$CH_{3}CH_{2}OH + Pb(OAc)_{4}$	10.52	2.61	0.80	1.64	OCH_2CH_3	
n-BuOH	10.52	2.53	0.90	1.62	O-n-Bu	34234-95-2
n-BuOH + Pb(OAc) ₄	10.61	2.57	0.90	1.62	O-n-Bu	
tert-BuOH	10.57	2.50	0.98	1.49	O-tert-Bu	34234 - 96 - 3
tert-BuOH + Pb(OAc) ₄	10.59	2.59	0.96	1.58	O-ten-Bu	
tert-BuOOH	10.57	2.50	0.95	1.49	O-tert-Bu	
^a In benzene at room temperature	. The splitt	ings are in gauss.	^b Ortho, par	ra, and meta H	's from N-phenyl gro	мp.

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phenyl radicals from triphenylbenzeneazomethane (Table III).

When a benzene solution of DPN with phenol present was irradiated, we obtained an esr spectrum with couplings A^{N} 10.61, $A_{o,p}^{H}$ 2.64 (3 H), A_{m}^{H} 0.93 (2 H), and A_{α}^{H} 1.80 G (1 H). The α -hydrogen splitting was of the same order as found for the nitroxide with RO groups attached at the α -carbon atom, and suggests that the phenoxyl group was trapped.

We also irradiated DPN solution in the presence of ethanol and hydrogen peroxide, expecting the esr signal of the nitroxide formed by trapping \cdot CH(OH)CH₃, but the spectra were complicated by the large concentration of benzoyloxy radical which formed.

Other Reactions.—When nitric oxide was briefly bubbled through a solution of DPN in benzene, the esr signal showed splittings $A^{\rm N}$ 10.63, $A_{o,p}^{\rm H}$ 2.62 (3 H), $A_{\rm m}^{\rm H}$ 0.96 (2 H), and $A_{\alpha}^{\rm H}$ 3.59 G (1 H), which were characteristic for phenyl radical scavenging. Apparently nitroxyl radical (NO·) abstracts a proton from the solvent, and the resultant phenyl radicals are



trapped. Treatment of PBN in an analagous manner yielded a strong signal characteristic of the benzoyloxy radical.

Most other substituted diphenylnitrones led to nitroxides analagous to those from DPN, when irradiated in the presence of alcohols, organolead, or -mercury reagents. For example, α -phenyl-N-p-chlorophenylnitrone with either ethanol or diethylmercury, in benzene, yielded on irradiation the esr spectra with splittings A^{N} 10.40, $A_{o,\alpha}^{H}$ 2.57 (3 H), and A_{m}^{H} 1.45 G (2 H). Under the same conditions α -(*p*-methoxyphenyl)-N-phenylnitrone gave A^{N} 10.70, $A_{o,p}^{II}$ 2.58 (3) H), $A_{\rm m}^{\rm H}$ 0.90 (2 H), and $A_{\alpha}^{\rm H}$ 1.65 G (1 H); and α phenyl- α -deuterio-N-phenylnitrone gave A^{N} 10.64, $A_{o,p}^{H}$ 2.57 (3 H), and A_{m}^{H} 0.93 G (2 H). Splittings due to the deuterium atom were not resolvable. However, α -phenyl- α -cyano-N-phenylnitrone failed to give any signal when treated as above. Only on irradiation of a benzene solution with tert-butyl hydroperoxide added was a signal observed. This stable signal showed splittings A^{N} 11.19, $A_{o,p}^{H}$ 2.37 (3 H), and A_{n}^{H} 0.80 (2 H), and may be due to the trapping of the tertbutoxy radical.



Figure 2.—Nitroxide radicals from α -phenyl-N-phenylnitrone. The stick patterns are based on coupling constants given in text: (a) from benzene solution containing methanol-lead tetraacetate; (b) from irradiation of benzene solution containing acetic acid and lead tetraacetate.

Discussion

In a deoxygenated solution of PBN in benzene containing the organometallics, Janzen and Blackburn established that alkyl radicals were generated and trapped by PBN.⁶ We observed that the presence of oxygen changes the scheme of the reaction. As noted earlier, we were able to trap only the XO+ radical with DPN and each organolead and -mercury compound, whereas with PBN two adduct radicals could be obtained. Partial deoxygenation gave rise to the XO adduct, while total removal of oxygen led to the trapping of R... The difference observed is probably related to the stability of the oxaziranes which are primary intermediates formed on irradiation of nitrones.¹⁰⁻¹² The relative stabilities are indicated by the fact that the oxazirane from PBN can be isolated. whereas the oxazirane from DPN has been identified only at low temperatures.

We previously concluded that oxygen was evolved



⁽¹⁰⁾ M. J. Kamlet and L. A. Kaplan, J. Oct. Chem., 22, 576 (1957).

⁽¹¹⁾ J. S. Splitter and M. Calvin, *ibid.*, 23, 651 (1958).
(12) K. Shinazawa and I. Tanaka, J. Phys. Chem., 68, 1205 (1964).

during the irradiation of nitrones,³ and other reports have indicated that irradiation of nitrones causes simple deoxygenation.¹³⁻¹⁵ Thus, in the case of DPN, it may not be possible to completely void oxygen from solution owing to this decomposition of the oxazirane.

It also appears that this oxygen effect may be limited to the nitrones. Experiments using 2-methyl-2nitrosobutanone-3 as a scavenger in poorly and well deoxygenated solutions led to the trapping of only one radical arising from alkyl radical scavenging.

We assign to these nitroxides formed from nitrones in partially oxygenated solutions a structure in which XO is attached at the α -carbon atom, and the XO group may be either an alkoxyl or an alkyl metal oxyl group. For example, with dimethylmercury additive, the XO may be either CH₃O or CH₃HgO. The splitting constants are almost identical with those found in the nitroxides with α -alkoxyl groups. However, differentiation between a nitroxide with an α -alkoxyl or α -alkyl metal oxyl group for the organometallic produced nitroxide is not feasible, since it is likely that either system would give splitting values of the same order. It is known that alkyl radicals react with other paramagnetic molecules, e.g., oxygen, as follows¹⁶

$$\mathrm{CH}_{3}\cdot \,+\, \mathrm{O}_{2} \longrightarrow \mathrm{CH}_{3}\mathrm{OO} \cdot \xrightarrow{\mathrm{CH}_{3}} \mathrm{CH}_{3}\mathrm{OOCH}_{3} \longrightarrow \mathrm{CH}_{3}\mathrm{O} \cdot$$

and that a similar type of reaction apparently occurs in the case of organometallic radicals.¹⁷

$$MeHg \cdot + O_2 \longrightarrow MeHgOO \cdot \xrightarrow{MeHg} MeHgOOHgMe \longrightarrow MeHgOO$$

Thus, either one of these oxygen-containing radicals could be trapped by the nitrone. It appears that this oxygen effect is seen only when nitrones are used as spin traps. Further work in this area is required to establish the structure of these nitroxides.

We assigned to those radicals formed by the irradiation of benzene solutions of the nitrones in the presence of alcohols, structures in which the alkoxyl group is joined at the α -carbon atom. The coupling constants obtained from PBN and DPN under these conditions are in good agreement with those obtained from the trapping of alkoxyl radicals generated by the treatment of alcohols with lead tetraacetate.7 The nitroxides in which alkyl and hydroxyalkyl groups are attached to the α carbon give much different coupling constants (Tables I-IV). Reactions of alcohols irradiated in the presence of scavengers has not been previously noted in the literature, and this reaction, which leads to nitroxide radical, appears to be limited to nitrones. We have not been able to obtain characteristic esr signals from the irradiation of 2-methyl-2-nitrosobutanone-3 in benzene solution with alcohol present. The reaction of the nitrones with alcohols described is probably not a radical trapping process, but rather an initial addition of the alcohol across the reactive $C = N \rightarrow O$ site, followed by conversion to the nitroxide.

We have observed an oxidation similar to that proposed for the adduct when N-benzoylphenylhydroxylamine in benzene is irradiated. The reactivity of the aldonitrone species to 1,3-addition reactions has been noted in the literature.¹⁸ The sluggishness of this reaction process with PBN as compared to DPN may be attributed to an inductive effect of the tert-butyl group, which would increase the electron density at the double bond and make the reaction site less attractive to the nucleophilic reagent.

The nitroxide formed by irradiation of a benzene solution of PBN with *tert*-butyl alcohol in the presence of hydrogen peroxide (Table II) is assigned the structure with $(-CH_2)(CH_3)_2COH$ joined at the α -carbon atom. The $(\cdot CH_2)(CH_3)_2COH$ radical is formed by abstraction of a β -hydrogen atom by \cdot OH radicals and has been observed previously under similar conditions.¹⁹

The production and trapping of phenyl radicals by DPN in the presence of nitric oxide in benzene was shown to occur by examination of the hfsc's, which were identical with those obtained from DPN and 1',1',1'triphenylbenzeneazomethane. Nitric oxide can behave as a radical quencher, but there is also evidence that nitric oxide will abstract hydrogen from stable molecules, and aryl radicals have been produced in the presence of nitric oxide.²⁰

Experimental Section

Chemicals.—2-tert-Butyl-3-phenyloxazirane and α -phenyl-Ntert-butylnitrone were prepared as described by Emmons²¹ and the α , N-diphenylnitrones according to the procedure of Wheeler and Gore.22

Dimethyl-, diethyl-, and diphenylmercury, triethyllead acetate, and tetra-n-butyllead were used as supplied by Alfa Inorganics. n-Butyllithium was obtained from Foote Mineral Co. and 1',1',1'-triphenylbenzeneazomethane was from Eastman Organic Chemicals.

Benzene was Baker and Adamson reagent redistilled and stored over sodium-lead alloy (dri-Na).

The alcohols were Spectrograde reagents used as supplied.

Generation and Measurement of Radicals .--- Solutions of the nitrones approximately $0.05 \ M$ in benzene were always freshly prepared. To 1 ml of the nitrone solution in a small glass sample vial, a drop or a few crystals of the organometallic compound was added, the solution was mixed, and then a portion was transferred into a 2-mm i.d. quartz esr cell. Deoxygenation was effected by passing a fine stream of argon bubbles through the solution by means of a drawn-out glass capillary. In this paper a partially deoxygenated solution was one that was treated for 10 min, and a totally deoxygenated solution was subjected to a 30min deaeration. Except as noted in the text, solutions were deaerated for 10 min.

The radicals formed from the nitrones in the presence of alcohols were obtained from 0.05 M solutions of the nitrone in benzene containing 1% of the alcohol. These solutions were deoxygenated for 10 min.

Irradiations of the solutions were carried out directly in a slotted cavity in the esr instrument, by exposing to the light of an un-

⁽¹³⁾ L. Alessandri, Atti Accad. Naz. Lincei, 19, 122 (1910); Chem. Abstr., 5, 276 (1911).

⁽¹⁴⁾ H. Shindo and B. Umezawa, Chem. Pharm. Bull., 10, 492 (1962).

⁽¹⁵⁾ M. Collonna, Gazz. Chim. Ital., 91, 34 (1961).
(16) E. W. R. Stacie, "Atomic and Free Radical Reactions," 2nd ed, Vol. II, Reinhold, New York, N. Y., 1954, Chapter VIII.

⁽¹⁷⁾ See review by N. J. Freswell and O. G. Gowenlock, Advan. Free Radical Chem., 1, 39 (1965); R. A. Jackson, ibid., 3, 231 (1969).

⁽¹⁸⁾ For example, see reviews: J. Hamer and A. Macaluso, Chem. Rev., 64, 473 (1964); G. R. Delpierre and M. Lamchen, Quart. Rev., Chem. Soc., 19, 329 (1965).

⁽¹⁹⁾ R. Livingston and H. Zeldes, J. Amer. Chem. Soc., 88, 4433 (1966). (20) Y. Rees and G. H. Williams, Advan. Free Radical Chem., 3, 199 (1969).

⁽²¹⁾ W. D. Emmons, J. Amer. Chem. Soc., 79, 5739 (1957).

⁽²²⁾ O. H. Wheeler and P. H. Gore, ibid., 78, 3363 (1956).

H Abstraction by *p*-Nitrophenyl Radical

filtered Bausch and Lomb SP 200-W super pressure mercury lamp for periods of 10 sec to 2 min. Spectra were measured at room temperature with a Varian V-4500 epr spectrometer equipped with a 9-in. magnet. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol.

Registry No.—Nitroxide from DPN + phenol, 34234-97-4; nitroxide from DPN + Ph₃CN=NPh, 34234-98-5; nitroxide from α -phenyl-*N*-*p*-chlorophenylnitrone + EtOH, 34234-99-6; nitroxide from α -phenyl-N-p-chlorophenyl nitrone + dimethylmercury, 342-35-00-2; nitroxide from α -(*p*-methoxyphenyl)-N-phenvlnitrone + EtOH, 34235-01-3; nitroxide from α - $(p-methoxyphenyl)-N-phenylnitrone + Et_2Hg, 34235$ nitroxide from α -phenyl- α -deuterio-N-phen-02-4:ylnitrone + EtOH, 34235-03-5; nitroxide from α -phenyl- α -deuterio-N-phenylnitrone + Et₂Hg, 34235-04-6; nitroxide from α -phenyl- α -cyano-N-phenylnitrone + tert-butyl peroxide, 34235-05-7; nitroxide from $PNB + Ph_2Hg$, 21572-75-8; nitroxide from DPN + Me₂Hg, 34235-07-9; nitroxide from DPN + Et_2Hg , 34235-08-0; nitroxide from DPN + Bu₄Pb, 34288-72-7.

Hydrogen Abstraction by the *p*-Nitrophenyl Radical^{1,2}

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The relative reactivities of a series of organic hydrogen donors were measured toward p-nitrophenyl radicals generated from p-nitrophenylazotriphenylmethane (NAT). The relative rate constants $k_{\rm H}$ for hydrogen abstraction from the donors are reported as $k_{\rm H}/k_{\rm Cl}$ values, where $k_{\rm Cl}$ is the rate constant for chlorine abstraction from CCl. The problems in calculation of $k_{\rm H}/k_{\rm Cl}$ values are discussed. Some ArH is produced from the ArN—NCPh₃ type initiators even in pure CCl₄ as solvent, and higher yields are produced at higher viscosities. It is shown that ArH is not a cage product. The ArH yields result from hydrogen abstraction from reactive hydrogen donors produced by the reaction of the ambident trityl radicals with radicals present in the system. These donors include XH from the reaction of trityl with Ar radicals and ZH from the reaction of trityl with a second trityl radical (see structures in paper). Two mechanisms are suggested to rationalize the viscosity effect; the more likely one assumes that XH is a cage product and, therefore, that higher yields of XH are produced at higher viscosities.

One of the most useful methods for probing the reactivity, polar nature, steric sensitivity, and other identifying features of free radicals is to measure their relative rate constants for hydrogen abstraction from a series of typical organic hydrogen donors. This approach has been used, for example, in studies of the phenyl radical,^{4,5} aromatic radicals,^{6a} the methyl radical,^{6b} and the hydrogen atom.⁷ A convenient method for determining such a series of relative rate constants involves generating the radical in a mixture of the hydrogen donor RH and carbon tetrachloride (eq 1 and 2). In this paper we report data obtained in this way for the phenyl and p-nitrophenyl radicals.

$$RH + Ar \cdot \xrightarrow{\kappa_{H}} R \cdot + ArH$$
(1)

$$\operatorname{CCl}_{4} + \operatorname{Ar} \cdot \xrightarrow{k_{\mathrm{Cl}}} \operatorname{CCl}_{3} \cdot + \operatorname{ArCl}$$
(2)

These radicals were generated by thermolysis at 60° of the appropriate phenylazotriphenylmethane (PAT) type of intiator, PAT itself for the phenyl radical and NAT, p-NO₂C₆H₄N=NCPh₈, for the p-nitrophenyl radical. We previously reported^{6a} some data for phenyl, *p*-bromophenyl, *p*-methylphenyl, and *p*-nitrophenyl,

(1) Reactions of Radicals. 42.

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and Bridger and Russell⁸ have reported extensive data for the phenyl radical. We here wish to clarify the cage chemistry of PAT-type initiators and also to report additional relative rate constants for hydrogen atom abstraction by the *p*-nitrophenyl radical.

Results and Discussion

The Cage Chemistry of PAT and NAT.-Cage processes have been particularly troublesome to $identify^{9-10}$ for PAT and similar initiators. Previously^{6a} we presented data on the yield of nitrobenzene (ArH) from NAT. We showed that the extrapolated yield of ArH appeared to be finite ($\sim 3\%$) at infinite dilution of NAT, in agreement with earlier reports on PAT,^{8,10a} and that the thermolysis of NAT in solvents of higher viscosity led to higher yields of ArH. These facts seemed to imply that ArH is a cage product. Arguments against ArH being a cage product are based on the observation that carbon disulfide or a solution of iodine in CCl₄ results in the elimination of ArH.^{11,12} It is now clear that the implication of these scavenging experiments is correct and that ArH is not a cage product.

Our evidence indicating that ArH is not a cage product can be summarized as follows. (1) Using a new, more sensitive gas chromatograph, we have been able

(10) (a) W. A. Pryor and H. Guard, J. Amer. Chem. Soc., 86, 1150 (1964);
(b) W. A. Pryor and K. Smith, *ibid.*, 89, 1741 (1967).

(11) Figure 3 of ref 6a.

(12) It is possible that a trace (<0.1%) of ArH is formed under these circumstances, but the amount is too small to estimate accurately

^{(3) (}a) John Simon Guggenheim Fellow, 1970-1971; (b) postdoctoral (a) John Simon Guggennenn Feinow, 1970-1971; (b) Postoretoria
 (b) Studenton an NIH grant, 1965; (c) Research Participant in an Atomic
 Energy Commission Research Participation Program, summer 1966.
 (4) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966,

⁽⁵⁾ A. F. Trotman-Dickenson, Advan. Free Radical Chem., 1, (1965).

 ^{(6) (}a) W. A. Pryor, J. T. Echols, Jr., and K. Smith, J. Amer. Chem. Soc.,
 88, 1189 (1966); (b) W. A. Pryor, D. F. Fuller, and J. P. Stanley, *ibid.*, in press.

⁽⁷⁾ W. A. Pryor, J. P. Stanley, and M. G. Griffith, Science, 169, 181 (1970); W. A. Pryor and J. P. Stanley, J. Amer. Chem. Soc., **93**, 1412 (1971); W. A. Pryor and R. W. Henderson, *ibid.*, **92**, 7234 (1970).

⁽⁸⁾ R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).
(9) (a) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Lett.*, 749 (1962); (b) D. H. Hey, M. J. Perkins, and G. H. Williams, *ibid.*, 445 (1963); (c) J. G. Garst and R. S. Cole, *ibid.*, 679 (1963); (d) G. A. Russell and R. F. Bridger, *ibid.*, 737 (1963).