$$O_2N-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-N(C_2H_5)_2 \xrightarrow[\text{butylamine}]{3660 \text{ Å}} HONH-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-N(C_2H_5)_2 \qquad (2)$$

$$\text{I} \qquad\qquad\qquad\qquad\qquad\qquad \text{III}$$

$$\text{III} + O_2 \longrightarrow (C_2H_5)_2N-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-\overset{\overset{O}{\uparrow}}{N}=N-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-N(C_2H_5)_2$$

$$\text{IV}$$

Anal. Calcd for $C_{32}H_{36}N_8O$: C, 70.04; H, 6.61; N, 20.42. Found: C, 69.76; H, 6.56; N, 20.31.

The absorption properties of the initially formed product and its oxidation to azoxy compound IV indicate that it is the hydroxylamine III. These results show that the photoreduction of I in butylamine occurs at the nitro group. The over-all process is shown in reaction 2.

Reduction of an aromatic nitro compound to a hydroxylamine and subsequent condensation to produce an azoxy compound were demonstrated in the photochemical reduction of nitrobenzene.[7] Oxidation of the initially formed hydroxylamine gave a nitroso compound, which reacted rapidly with the hydroxylamine to give an azoxy compound.[7-9] It is interesting to note that IV is readily formed from III by a similar process, even when the concentrations of the reactants are as low as 10^{-4} M. The quantum yields for the photoreduction of I under various conditions are shown in Table I.

Table I. Photoreduction of I[a] under Various Conditions with 3660-Å Light[b]

| Solvent | Additive | | |
	Compd	Concn, M	Φ_D[c]
Isopropyl alcohol	None		1.4×10^{-4}
	Benzophenone	0.27	0.05
	Fluoren-9-one	0.025	$<1 \times 10^{-4}$
Butylamine	None		4.2×10^{-4}
	Benzophenone	0.27	0.14
	Fluoren-9-one	0.025	6.0×10^{-3}

[a] Concentration of I was 2.2–2.4 $\times$ 10^{-4} M. [b] A Bausch and Lomb Model 33-86-07 high-intensity grating monochromator was used for these experiments. The light source was an Osram HBO 200-W lamp. The intensity of the incident light as determined by ferroxalate actinometry [C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), A235, 518 (1956)] was 3.0 $\times$ 10^{-6} einstein/min for experiments without sensitizers and was 4.8 $\times$ 10^{-1} einstein/min for all others. [c] Over-all quantum yield for the initial 10% degradation of I.

The formation of IV as a product from photolysis of I in butylamine suggests a mechanism different from that for the reaction in alcohol solvent. Recent studies[10-13] on the photoreduction of aromatic ketones in amine solvents have presented evidence for reduction by a mechanism involving an initial electron transfer from the amine to the excited triplet state of the ketone, followed by a proton transfer and electron redistribution. The over-all process produced the corresponding pinacol in high yield. Selective reduction of the nitro group of I

(7) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, 88, 4330 (1966).
(8) Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *ibid.*, 86, 3854 (1964).
(9) G. A. Russell and E. J. Geels, *ibid.*, 87, 122 (1965).
(10) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).
(11) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 90, 165 (1968).
(12) S. G. Cohen and J. I. Cohen, *ibid.*, 89, 164 (1967).
(13) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 72, 3782 (1968).

in butylamine can be rationalized in terms of a similar electron-transfer process. Since the electron density in the initially formed radical anion of I may be expected to be greater on oxygen than on the azo nitrogen,[14] proton transfer from the amine radical cation to oxygen would follow.

It is interesting to note that a similar process occurred when either benzophenone or fluoren-9-one was used as sensitizer. These results indicate that both the initially formed benzophenone ketyl radical anion and the fluorenone ketyl radical anion transfer an electron rapidly to I before proton transfer from the amine radical cation occurs.[17] Products resulting from interaction of the ketyl radical with I would be formed if proton transfer to the ketyl radical anion competed significantly with electron transfer to I. The photolysis of I (0.01 M) in a 0.5 M solution of benzophenone in butylamine gave a 97% yield of IV (isolated), and photolysis under conditions where the concentration of I was 2.4 $\times$ 10^{-4} M gave a yield of about 96% (determined spectrophotometrically). Thus, at the two extreme concentrations, no appreciable quantity of II was formed.

The low quantum yield obtained for the reduction of I in the presence of benzophenone (lower than 0.9[13]) may be due in part to reaction 3.

$$ArNO_2\cdot^- + \overset{+\cdot}{R}NH_2 \longrightarrow ArNO_2 + RNH_2 \qquad (3)$$

(14) The esr spectrum of the radical anion of I in tetrahydrofuran (sodium counterion), although not fully resolved, was similar to spectra reported for *para*-substituted nitrobenzene radical anions (a_n = 9.8 G).[15,16]
(15) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 89, 300 (1967).
(16) E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, 32, 820 (1967).
(17) To show that electron transfer from the benzophenone ketyl radical anion to I was a favorable process, a solution of sodium benzophenone ketyl in tetrahydrofuran (1.0 $\times$ 10^{-4} M) was added to an equivalent quantity of I through a break seal. The initial esr spectrum of the benzophenone ketyl was replaced by that of the radical anion of I. No evidence was seen in the resulting spectrum for the presence of benzophenone ketyl, thus indicating that electron transfer to I is an energetically favored process.

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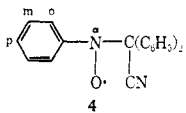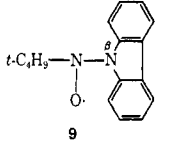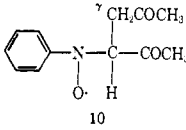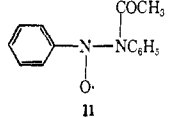*Division of Eastman Kodak Company*
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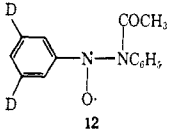
Electron Spin Resonance Studies on Oxidation with Nickel Peroxide. Spin Trapping of Free-Radical Intermediates

Sir:

During the course of an investigation on the mechanism of oxidation with nickel peroxide[1] it became de-

Table I. Spin Adducts in the Oxidation with Nickel Peroxide[a]

Substrate	Radical scavenger	Nitroxide	g value[b]	Hyperfine splitting constant,[b] G						
				a_α^N	a_o^H	a_m^H	a_p^H	a_β^H	a_β^N	a^H
Diphenyl-acetonitrile	Nitrosobenzene	4	2.00575	11.10	2.36	0.90	2.36			0.2[c]
Carbazole	2-Methyl-2-nitro-sopropane	9	2.00587	16.77					1.37	
Acetonyl-acetone	Nitrosobenzene	10	2.00569	10.75	2.75	0.97	2.75	2.42		{0.51[d] 0.26[d]}
Acetanilide	Nitrosobenzene	11	2.00536	11.61[e]	{2.60[e] 2.73[e]}	0.89[e]	2.60[e]			1.67[e]
Acetanilide	3,5-Dideuterio-nitrosobenzene	12	2.00530	11.63	2.67		2.67			1.70

[a] A Varian V4502-15 epr spectrometer was used with 100-kHz field modulation. [b] Values in benzene. [c] Interaction with one or three unidentified protons. [d] May be due to unequivalent γ protons. [e] Values from G. Binsch and C. Rüchardt, J. Amer. Chem. Soc., 88, 173 (1966). [f] Hfs of deuteriums is not resolved.

sirable to detect and to identify free radicals as reaction intermediates. There have been some attempts[2-5]
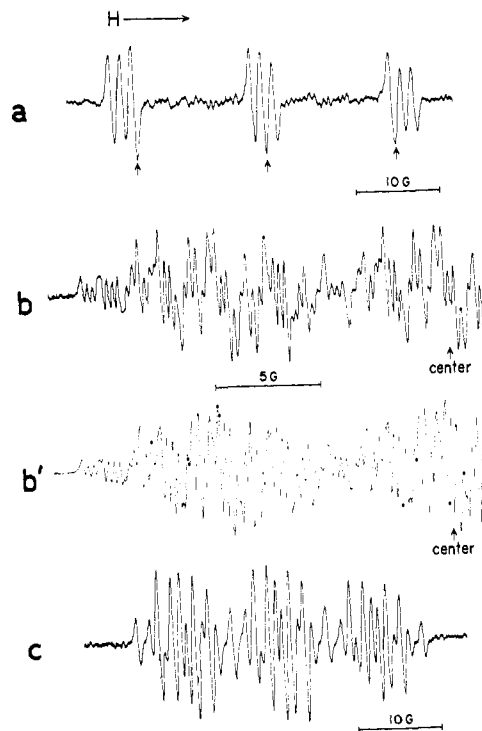

Figure 1. Esr spectra of nitroxides 9 (a), 10 (b), and 12 (c), and a simulated spectrum (b') of 10. Arrows in spectrum a indicate a superposition of the spectrum due to a trace of di-t-butylnitroxide.
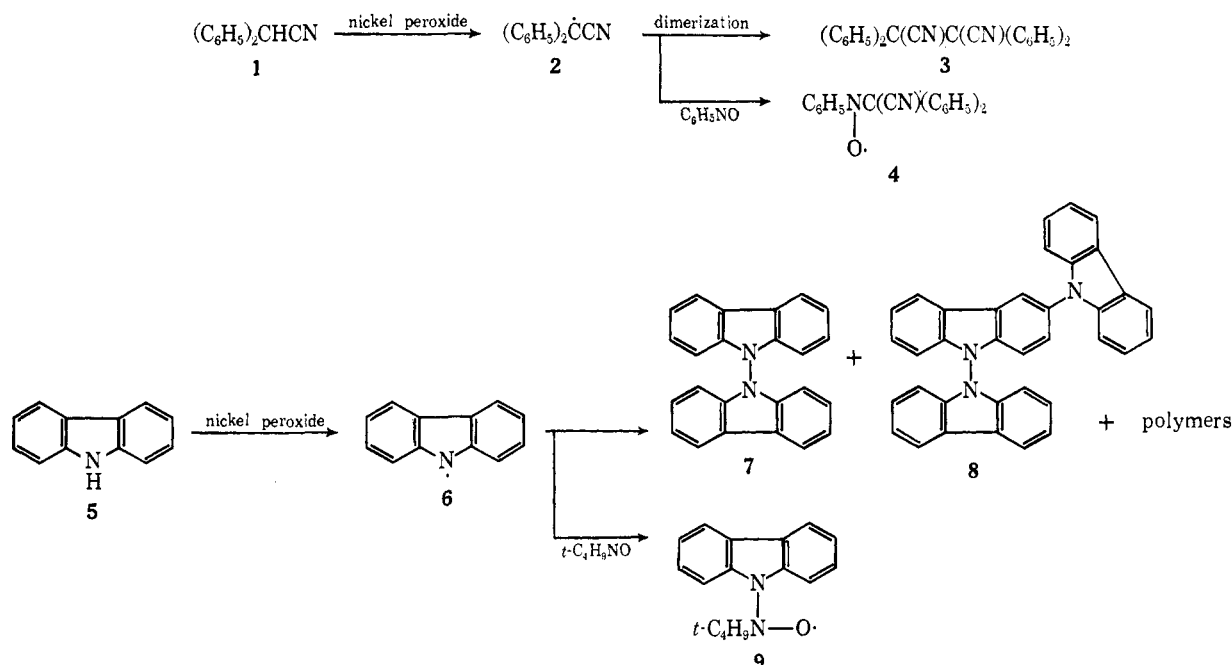
to apply an electron spin resonance (esr) trapping technique to study the short-lived free radicals without using flow-system techniques. This new method does not need any rapid radical-forming reactions, and large volumes of materials are not required. A nitroso compound[2,4,6] such as 2-methyl-2-nitrosopropane, or a nitrone[3,5,7] such as phenyl-t-butylnitrone, have been reported as effective radical scavengers.

This work was undertaken to explore the application of this technique to oxidation reactions with nickel peroxide. This reagent is represented by the empirical formula $NiO_{2.77}H_{2.85}$ and is a black amorphous powder with the tendency to abstract hydrogens from organic compounds.[1] Using nitrosobenzene and 2-methyl-2-nitrosopropane as radical scavengers, we could readily detect short-lived intermediates as nitroxides (spin adducts) and define the structures of trapped radicals by esr spectroscopy.

In the presence of a nitroso compound (0.05-0.1 M), a substrate (0.05-0.5 M) was oxidized with nickel peroxide (0.2-1 equiv amounts of the substrate) in deoxygenated benzene at room temperature for 10-30 sec, and the esr spectrum was immediately recorded at room temperature. Typical examples of the nitroxides formed in the oxidation reactions of a variety of sub-

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strates are collected in Table I with g values and the coupling constants. The structures of the nitroxides are reasonably deduced from their esr spectra. The nitroxides that were studied were stable and decay of their spectra was hardly noticed during the esr measurements. None of the nitroxides given in Table I was produced if a substrate, nitroso compound, or nickel peroxide was absent.[8]

The oxidation of diphenylacetonitrile (1) with 0.5 equiv of nickel peroxide resulted in an almost quantitative yield of tetraphenylsuccinonitrile (3).[1] The cyanodiphenylmethyl radical (2) is considered as an intermediate in this reaction, while the detection of nitroxide 4 in the presence of nitrosobenzene indicates that 2 is trapped by nitrosobenzene.

The oxidation of carbazole (5) with nickel peroxide in the presence of 2-methyl-2-nitrosopropane in the absence of light afforded an esr spectrum (Figure 1a) consisting of a triplet of triplets having equal intensity which was attributed to nitroxide 9. Since the oxidation products of 5 with nickel peroxide are N,N'-dicarbazolyl (7) and 3-(N-carbazolyl)-N,N'-dicarbazolyl (8) along with some polymers,[9] detection of nitroxide 9 gives proof of the existence of the N-carbazolyl radical (6) in the course of the reaction.

The esr spectrum (Figure 1b) of nitroxide 10 obtained in the oxidation of acetonylacetone shows a hyperfine splitting (2.42 G) by one β proton with respect to the nitrogen atom. This observation implies that the hydrogen abstraction is not from the methyl group of acetonylacetone but from the methylene group.

The stable radical detected by esr during the decomposition of N-nitrosoacetanilide in benzene was presumed to be the phenyldiazotate radical by Binsch and Rüchardt,[10] but later Chalfont and Perkins[11] proposed that it had a nitroxide structure (11), and this view was

(8) A very weak phenylnitroxide esr spectrum, in most cases, was observed in mixing the substrate and nitrosobenzene at room temperature. It is supposed that nitrosobenzene abstracted a hydrogen from the substrate to form phenylnitroxide.
(9) J. Sugita, Nippon Kagaku Zasshi, 88, 659 (1967).
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(11) G. R. Chalfont and M. J. Perkins, J. Amer. Chem. Soc., 89, 3054 (1967).

strongly supported by Forrester.[12] The same esr spectrum as reported by Binsch and Rüchardt was obtained in the oxidation of acetanilide with nickel peroxide in the presence of nitrosobenzene. This result confirms the proposal of Chalfont and Perkins. The hyperfine splitting constant of the β nitrogen is obvious from the spectrum (Figure 1c) recorded when 3,5-dideuterionitrosobenzene was used as a radical trap instead of nitrosobenzene. The results obtained from the oxidation of phenols, alkylbenzenes, and other amines with nickel peroxide by means of this spin-trapping technique will be reported later.

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The Synthesis and Solvolysis of
endo-Bicyclo[3.2.1]-oct-6-en-8-yl Tosylate

Sir:

Although the unusual reactivity ($k_I/k_{II} = 10^{11}$) of the anti-7-norbornenyl system was first reported more than 10 years ago,[1] interest in it and related systems still remains high.[2,3] However, most of the recent interest has been centered on the actual structure of the nonclassical 7-norbornenyl ion. Only one report has been made concerning the geometry necessary for participation of the double bond with the developing cationic center in the cyclopentene ring. Bartlett and Rice

(1) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, J. Amer. Chem. Soc., 77, 4183 (1955); (b) S. Winstein and M. Shatavsky, ibid., 78, 592 (1956).
(2) (a) P. G. Gassman and A. F. Fentiman, Jr., ibid., 91, 1545 (1969); (b) J. J. Tufariello and R. J. Lorence, ibid., 91, 1546 (1969); (c) J. Lhomme, A. Diaz, and S. Winstein, ibid., 91, 1548 (1969); (d) P. G. Gassman and D. S. Patton, ibid., 91, 2160 (1969).
(3) Y. Hata and H. Tanida, ibid., 91, 1170 (1969).