essentially the same spectrum by mixing benzene solutions of nitrosobenzene and N-bromoacetanilide (Figure 2). We consider that the most probable structure for the radical responsible for this spectrum is therefore **3**; in the second reaction this is considered to arise by addition of the nitrogen-centered radical **4** to nitrosobenzene (eq 9).[16] The ^{15}N experiments already cited[14] once more allow assignment of the larger nitrogen coupling in radical **3** to the nitrogen atom bonded to oxygen. The value of 11.7 gauss seems very reasonable for nitrogen in this environment, by analogy with other data on nitroxide radicals.[17]

$$\underset{\mathbf{4}}{\mathrm{Ph\dot{N}COCH_3}} + \mathrm{PhN{=}O} \longrightarrow \mathbf{3} \qquad (9)$$

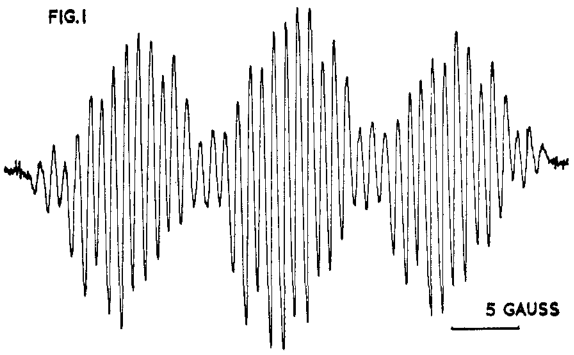
Reaction of N-bromo-*p*-chloroacetanilide with nitrosobenzene gives a radical whose esr spectrum is indistinguishable from that of **3**, consistent with the hypothesis of negligible splitting by the ring B protons. Reactions of N-bromoacetanilide with *p*-chloronitrosobenzene, *p*-nitrosotoluene, and 2-methyl-2-nitrosopropane also give stable radical species, the esr spectra of which have been resolved into 50, 42, and 9 lines, respectively.[18] These reactions appear to constitute the first examples of addition of organic nitrogen-centered radicals to the nitroso group, though there are now numerous reports of additions by carbon-[19] and oxygen-centered[20] radicals.

Assuming that structure **3** correctly represents the structure of the stable radical in the nitrosoacetanilide reaction, this species could then adopt the role of oxidant in a modified mechanism such as that outlined below. This finds close analogy with the mechanism proposed for the decomposition of benzoyl peroxide in the presence of diphenyl nitroxide.[15]

Initiation

$$\mathrm{PhN{=}NOCOCH_3} \longrightarrow \mathrm{Ph\cdot} + \mathrm{N_2} + \mathrm{\cdot OCOCH_3} \qquad (10)$$

$$\mathrm{Ph\cdot} + \mathbf{1} \longrightarrow \mathbf{3} \qquad (8)$$



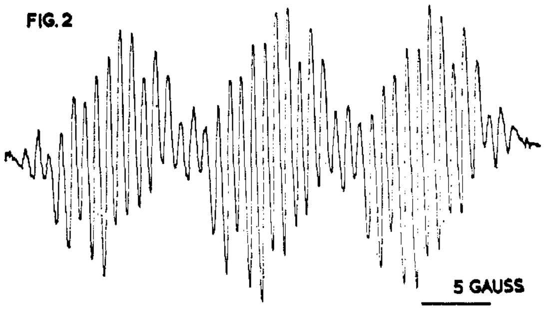
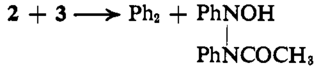


Figure 1. Esr spectrum of the radical formed during the decomposition of N-nitrosoacetanilide in benzene.

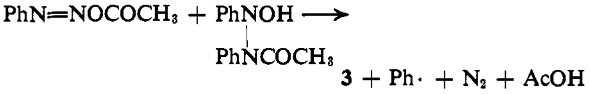
Figure 2. Esr spectrum of the radical formed on mixing benzene solutions of N-bromoacetanilide and nitrosobenzene.

Main product-forming sequence

$$\mathrm{Ph\cdot} + \mathrm{PhH} \longrightarrow \mathbf{2} \qquad (5)$$

 (11)

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathrm{Ph_2} + \underset{\mathrm{Ph\dot{N}COCH_3}}{\mathrm{PhNOH}} \qquad (11)$$

 (12)

$$\mathrm{PhN{=}NOCOCH_3} + \underset{\mathrm{PhNCOCH_3}}{\mathrm{PhNOH}} \longrightarrow \mathbf{3} + \mathrm{Ph\cdot} + \mathrm{N_2} + \mathrm{AcOH} \qquad (12)$$

Reaction 12 may represent more than one discrete step. The reduced yield of biphenyl with high initial concentrations of nitrosoamide might be explained in terms of increased removal of phenyl radicals in reaction 8, leading to unidentified by-products.

Other examples of phenylation reactions in which product formation is dominated by the presence of relatively stable radical intermediates have also been documented.[21] In the light of the present work, the identity of any such species in the Gomberg reaction[11] merits reinvestigation.

Acknowledgment. We thank the Science Research Council for financial support (to G. R. C.), and Professor D. H. Hey for valuable discussions.

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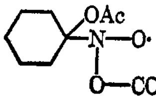
[16] The esr spectrum developed on mixing the reagents, though photolysis of the bromo amide by stray laboratory light may have been instrumental in radical production. At room temperature, the presence of silver powder did not increase the radical concentration. In a control experiment, no radical spectrum was formed from nitrosobenzene and molecular bromine. Spectra were recorded on a modified Varian V4502 spectrometer generously placed at our disposal by Dr. G. R. Wilkinson of the Physics Department of this college. We are also indebted to Dr. Yvonne Rees for a helpful appraisal of various sources of phenylacetamido radicals.

[17] For example, compound i has $a_N = 16.2$ gauss in methylene chloride: J. W. Lown, *J. Chem. Soc., Sect. B*, 441 (1966). This value might be expected to be reduced slightly in 3 by delocalization of the unpaired electron over the aromatic ring (*cf.* ref 18).



i

[18] The last of these (nine lines) appeared as a triplet of triplets (a_N = *ca.* 16 and 1.5 gauss) and is ascribed to *t*-BuN(O·)N(Ph)COCH$_3$. This radical has not yet been obtained free from di-*t*-butyl nitroxide, despite attempts to avoid direct photolysis of the nitrosobutane (see ref 19). The spectrum in Figure 1 has been analyzed in detail[13,14] and involves considerable coincidence of lines. There must also be coincidences in the spectra of the chloro- and methyl-substituted radicals and analysis of the spectra of these and related nitroxides will be given in the full paper.

[19] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1966), and references therein.

[20] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *ibid.*, 385 (1967).

[21] D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 110 (1965); M. J. Perkins, *ibid.*, 5932 (1964).

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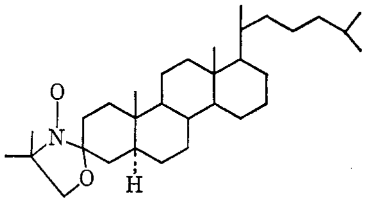
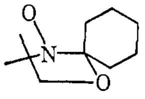
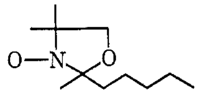
A New Versatile Ketone Spin Label

Sir:

The study of molecular systems by esr spectroscopy is contingent on the presence within the system of un-

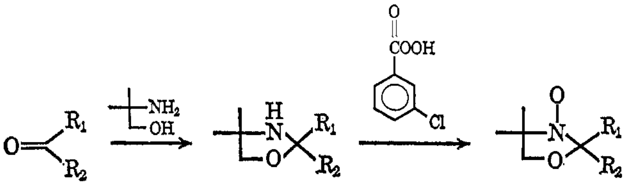
Table I. Physical and Spectral Data

Nitroxide	Mp or bp (mm), °C	a_N,[a] ±0.1 gauss	g value, ±0.0002	λ_{max}, mμ (ε)	% yield
 1	175–176 (methanol–ether)	14.3	2.0058	443 (7.2) (ether)	70[b]
 2	57–58 (pentane)	14.3	2.0058	420 (7.4) (ethanol)	42[c]
 3	~70 (0.08)	14.4	2.0058	422 (7.0) (ethanol)	26[c,d]

[a] X-band esr spectra were measured in ethyl acetate solution (*ca.* 5 × 10^{-4} *M*) and consisted of the usual three-line nitroxide spectra. All three nitroxides were found to have 1.0 ± 0.2 spins per molecule. [b] This represents pure crystalline material. [c] Yields were determined by visible absorption spectroscopy. [d] The analytical specimen was obtained by preparative vapor phase chromatography.

paired electron spins. Elegant methods have recently been developed for the chemical attachment of relatively stable nitroxide free radicals to diamagnetic biomolecules, permitting study of the latter by esr techniques. Several workers have applied this spin-labeling method with notable success to the study of proteins such as bovine serum albumin.[1]

The continuing successful development of this technique depends to a large measure on the availability of a wide variety of spin-label molecules. We wish to report the first general method for converting ketones to stable nitroxide free radicals. The reaction sequence from the ketone to the nitroxide is outlined below.



For example, refluxing a toluene solution of cholestan-3-one containing an excess of 2-amino-2-methylpropan-1-ol[2] and a trace of *p*-toluenesulfonic acid monohydrate for several hours with continuous water removal by means of a Dean–Stark trap led to the corresponding oxazolidine, one epimer of which had mp 124–125°.[3] The known[4] oxazolidines derived from cyclohexanone and heptan-2-one were similarly prepared.

In each instance oxidation of the oxazolidine to the corresponding nitroxide was effected by dropwise addition over 20 min of an ether solution of 1.50 equiv of *m*-chloroperbenzoic acid to an ice-cold, stirred ether solution of oxazolidine. The resulting solution was allowed to stand at 25° for 24 hr. The ether layer was washed with cold 5% sodium bicarbonate solution and dried over magnesium sulfate, and the solvent was removed under vacuum, affording the nitroxide. Table I summarizes pertinent physical and spectral data for the three representative nitroxides **1**, **2**, and **3**.

The conformationally rather rigid nature of the oxazolidine ring system in these new spin labels should markedly facilitate the interpretation of rotational correlation times in terms of the local environment of the spin label.

Acknowledgments. We thank Professor O. H. Griffith for determination of the esr spectral data and the National Science Foundation (Grant GP5805) and the Office of Scientific and Scholarly Research of the Graduate School of the University of Oregon for financial support of this work.

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(1) T. J. Stone, T. Buckman, P. L. Nordio, and H. M. McConnell, *Proc. Natl. Acad. Sci. U. S.*, 54, 1010 (1965); O. H. Griffith and H. M. McConnell, *ibid.*, 55, 8 (1966); L. Stryer and O. H. Griffith, *ibid.*, 54, 1785 (1965).

(2) Available from Aldrich Chemical Co.

(3) All new compounds gave carbon, hydrogen, and nitrogen elemental analyses within 0.3% of the theoretical values.

(4) E. M. Hancock and A. C. Cope, *J. Am. Chem. Soc.*, 66, 1738 (1944).

Concerning the Anion and Cation Radicals of Corannulene

Sir:

The consideration of valence bond structures such as **2** for the recently synthesized strained, nonalternate benzoid hydrocarbon, corannulene (**1**),[1] intimated the theoretical accessibility of the corresponding radical anion and radical cation derivatives. The unusual polar form **2** implies that the radical cation and anion correspondingly will have large contributions of structures such as **3** and **4** to the resonance hybrid. Because of the importance of these species to more sophisticated computations on the corannulene molecule, as

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(1) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, **88**, 380 (1966).