Table VI. Characteristics of Compounds

Compd R =	δ (ppm) in nmr[a]			Retention time in glpc, min[b]
	$CH_3CH_2C=$	$HC=$	$-CH_2O$	
trans-$R(C_2H_5)C=CHCH_2OH$				
n-C_4H_9	2.00	5.35	4.02	7.5
n-C_5H_{11}	2.00	5.25	4.01	11.1
n-C_7H_{15}	2.00	5.25	4.01	25.4

[a] See Table III, footnote *a*. [b] See Table III, footnote *c*.

trans-3-Alkyl-2-alkenyl Pyrophosphates. *trans*-3-Alkyl-2-alkenyl alcohols were phosphorylated in a 1-mmol scale essentially by the method of Cramer and Böhm[9] as modified by Kandutsch, *et al.*[10] To the reaction mixture of the phosphorylation was added 5 ml of ether, and the mixture was extracted four times with 1-ml portions of 1% aqueous ammonia. After the combined aqueous extract was washed four times with 5-ml portions of ether, 0.5 ml of cyclohexylamine was added. Then the solution was made *ca.* 50% acetone–water by the addition of acetone and allowed to stand at 4° overnight. After removal of the crystalline monophosphate cyclohexylammonium salt by filtration, a few drops of a saturated lithium chloride solution were added to the filtrate. After standing for several hours at 4°, the precipitate of the lithium salt of the pyrophosphate ester was collected by filtration and washed with a small volume of ice-cooled 50% acetone–water and then with a few drops of cold water. The ir spectrum indicated that this precipitate was almost free from the monophosphate ester. The contamination with the monophosphate was checked mainly on the basis of the fact that the lithium salts of the pyrophosphates showed absorptions at 1115–1125, 930–940, and 720–735 cm^{-1} and the lithium salts of the monophosphates at 1100–1160 and 1010–1030 cm^{-1}.

trans-2-Alkenyl pyrophosphates were obtained similarly from *trans*-2-alkenols synthesized by the malonic acid condensation of the corresponding aldehydes.

Enzymatic Reaction. In the standard experiments, the incubation mixture contained, in a final volume of 1.0 ml, 40 μmol of phosphate buffer, pH 7.0, 5 μmol of magnesium chloride, 25 nmol of [^{14}C]isopentenyl pyrophosphate (30 nCi), 25 nmol of an allylic pyrophosphate to be examined, and 0.1 mg of the enzyme. After the mixture had been incubated at 37° for 30 min, the reaction was stopped by the addition of 0.3 ml of 1 *N* hydrochloric acid, and the mixture was incubated at the same temperature for 15 min to complete the hydrolysis of allylic pyrophosphates. The mixture was made alkaline with 0.35 ml of 1 *N* sodium hydroxide, and extracted with 5 ml of *n*-hexane. After washing with water the radioactivity in the extracts was determined in a toluene scintillator with a Kobekogyo liquid scintillation counter GCL-111. The efficiency of counting ^{14}C was 86%.

Analysis of Products. For preparing the samples for gas chromatographic analysis, large scale incubations (three–ten times as much as the standard incubation) were made for 2 hr. The reaction mixture was then adjusted to pH 9.0 with Tris–HCl buffer, and intestinal alkaline phosphatase (10 μl, Boehringer, grade II, 10 mg/ml) was added. After the incubation at 37° for 3 hr, the mixture was extracted with petroleum ether. The extracts were subjected to gas chromatographic analysis. The analysis was carried out with a Shimadzu radiogas chromatograph RID at linear programmed temperature at a rate of 4°/min from 140 to 245° on a 1-m column packed with PEG 20M on Chromosorb AW. Helium gas was used as a carrier at a rate of 30 ml/min. A mixture of prenols (geraniol, farnesol, and geranylgeraniol) was usually used for the reference.

In the mixed incubation in Figure 3, the incubation mixture contained the same as that in the standard incubation except that 25 nmol of *trans*-3-methyl-2-octenyl pyrophosphate was added in addition to *trans*-3-methyl-2-pentenyl pyrophosphate. After incubation for 35 min, the products were analyzed as described above.

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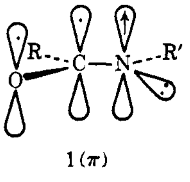
Communications to the Editor

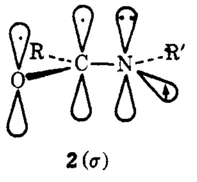
Nitrogen-Centered Free Radicals. V. Electron Spin Resonance Evidence for a π Electronic Ground State of Transient Amido Free Radicals[1]

Sir:

We wish to report the first unequivocal identification of simple amido radicals, R–CO–Ṅ–R′, by electron spin resonance spectroscopy. Amido radicals have been the subject of considerable controversy due to the possibility of either a π or σ electronic ground state for this type of radical (*cf.* **1** and **2**). The basic question has been whether the difference in energy resulting from the delocalization of a pair of electrons in a p orbital would be sufficiently great to overcome the promotional energy of an electron in a hybrid orbital to the p orbital. Purported evidence for both a π[2–6] and a σ[7–10] structure



1 (π)



2 (σ)

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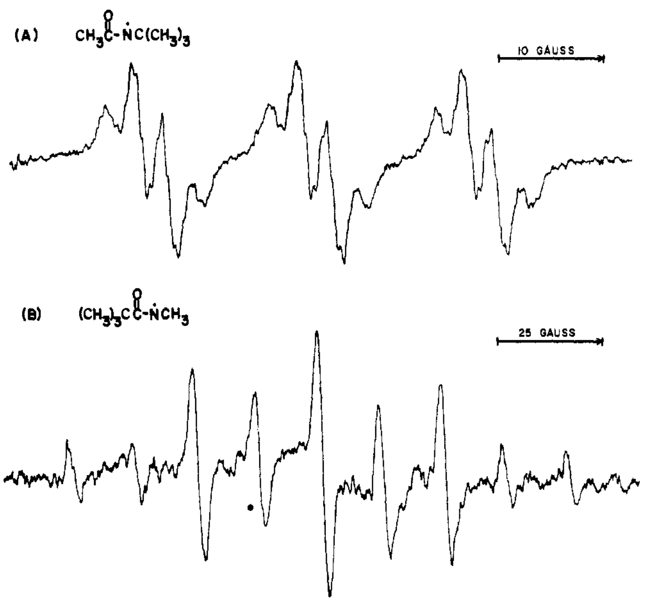

Figure 1. Esr spectra of (A) $CH_3CO\dot{N}C(CH_3)_3$ and (B) $(CH_3)_3CCO\dot{N}CH_3$ in cyclopropane solution at −40 and −100°, respectively. The partially resolved splittings in (A) result from interaction with the hydrogens of the *tert*-butyl substituent.

has been reported but the literature is confusing and frequent misassignments of spectra have occurred. The most reliable evidence suggests that the nitrogen-centered radical derived from urea,[2] $H_2N-CO-\dot{N}H$, is best described as a π radical but the electron-donating NH_2 must interact strongly with the carbonyl group to effectively dampen its electron-withdrawing capability and this species cannot be considered truly representative of simple amido radicals. Likewise, *N-tert*-butoxyamido radicals, $R-CO-\dot{N}-O-t\text{-}Bu$, have been investigated[4] but the alkoxy substituent attached directly to nitrogen could conceivably bias these species in favor of a π structure.

In Table I are listed the esr spectral parameters for two simple amido radicals generated by photolysis of the corresponding *N*-chloramides in cyclopropane directly in the cavity of the esr spectrometer.[11] The esr spectra are shown in Figure 1. The derived data are typical of those for a π electronic ground state **1** rather than a σ structure **2**. The magnitudes of a^N and $a^H_{CH_3}$ are consistent with other nitrogen-centered π radicals[2,4,12–14] and suggest that there is not extensive delocalization of the unpaired electron onto the carbonyl group.[15] A σ radical such as **2** would be expected to exhibit a much greater a^N since the unpaired electron would reside in an orbital of appreciable s character. For example, σ-iminoxyl radicals have a^N values of about 30 G even though the spin density at nitrogen is only about 0.5.[16,17]

Table I. Hyperfine Splitting Constants and *g* Values for Amido Radicals and Related Nitroxides[a]

Radical	a^N	a^H	*g* value[b]	Temp, °C
$(CH_3)_3C\overset{O}{\overset{\|}{C}}\dot{N}CH_3$	15.00	29.30[c]	2.0053	−100
$CH_3\overset{O}{\overset{\|}{C}}\dot{N}C(CH_3)_3$	15.70	2.71[c]	2.0044	−40
$CH_3\overset{O}{\overset{\|}{C}}—\overset{O\cdot}{\overset{\mid}{N}}C(CH_3)_3$	7.57		2.0066	−90
$CH_3\overset{O}{\overset{\|}{C}}—\overset{O\cdot}{\overset{\mid}{N}}CH_3$	7.20	8.53[c]	2.0065	−90

[a] Spectra of the amido radicals were recorded in cyclopropane solution; the nitroxides were generated in air-saturated toluene solution. Estimated accuracy of coupling constants is ±0.7%. [b] Corrected for second-order effects; estimated accuracy is ±0.0001. [c] Interaction with 3 H.

By photolyzing *N*-chloramides in air-saturated toluene solutions, spectra of the corresponding nitroxides are observed. The identity of these radicals is evidenced by the mode of generation, the relatively small a^N and $a^H_{NCH_3}$ coupling constants, the *g* values characteristic of nitroxides, the enhanced stability as compared to the transient amido radicals, and comparison to reported acyl nitroxides.[18,19] The present results indicate quite clearly that the paramagnetic species recently reported by Tordo, *et al.*,[3] and interpreted as amido radicals are instead the corresponding acyl nitroxides. We are presently investigating other amido radicals and will report additional results in the full publication of this work.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 5579-AC4), and the Kansas State University Bureau of General Research for support of this work.

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[11] A PEK AH6-2B, 2000-W high-pressure mercury capillary lamp was utilized in conjunction with a suitable lens system.

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[17] The *g* values for the amido radicals are also reasonable for a π electronic structure although the reason(s) for the difference in *g* values between the first two entries in Table I is not immediately apparent.

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Received June 17, 1972

Generation of Boron-Stabilized Carbanions

Sir:

The electronic configuration of trivalent boron is similar to that of carbon in a carbonyl grouping and many of the reactions of aldehydes or ketones have counterparts in the reactions of organoboranes.[1] Treatment of an aldehyde or a ketone possessing α hydrogens with base furnishes a carbonyl-stabilized anion (eq 1). Subsequent reactions of these enolate anions provide some of the most useful and versatile

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[1] For example, the Baeyer–Villiger oxidation and the Beckmann rearrangement of ketones are strikingly similar to the peroxide oxidation[2] and amination[3] reactions of organoboranes.

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