1 ($C_{24}H_{39}NO_6$), mp 159–160°, followed by oxidation with Cornforth reagent gave **7** as well as the 1,14-diketo derivative **8** ($C_{24}H_{35}NO_6$), mp 170–171°, ν_{max} 1740 and 1690 cm^{-1}. The diketo derivative **8** was reduced with 1 equiv of sodium borohydride to a product which is identical with **7** by ir, nmr, melting point, and mixture melting point. The stereo-specificity of this reduction is anticipated, because the β side of the 14-keto group is less hindered, thereby favoring an α-oriented 14-hydroxyl group. Similar arguments cannot be applied to the reduction of the 1-keto function where both sides are essentially equally hindered. Reduction of **7** with sodium borohydride proceeded without stereo-specifity, to afford a mixture of two epimeric triols **1** and **4** in a ratio of 1:2, respectively, which could be separated by preparative tlc over silica gel. The less polar triol **4** crystallized from chloroform, as a chloroformate, mp 100–105°, $[\alpha]^{26}D$ +6.0° (*c* 5.3, ethanol). The more polar epimer was shown to be identical with the hydrolysis product of delphisine by ir, nmr, melting point, and mixture melting point and therefore may be assigned structure **1.**

The ir spectra of the epimeric triols **1** and **4** were different, especially in the hydroxyl region. Triol **1** showed broad absorption between 3620 and 3000 cm^{-1}, with a sharp peak at 3515 and well-defined peak at 3290 cm^{-1}, indicative of a hydrogen bonded hydroxyl group. In contrast triol **4** showed hydroxyl absorption between 3600 and 3210 cm^{-1} centered at 3430 cm^{-1}. The nmr spectra of the triols were also different, especially the signals of the C-1 protons. Compound **1** displayed a multiplet at δ 3.82; compound **4** showed a multiplet at δ 4.00.

Both triols formed triacetates with acetic anhydride and *p*-toluenesulfonic acid. Epimer **1** gave 1α,8β,14α-triacetate, mp 151°, identical with delphisine 1α-monoacetate. Its nmr spectrum shows an *N*-ethyl group (3 H triplet, J = 7 Hz) centered at δ 1.12, three acetoxyl groups (δ 2.05 as 3 H singlet and δ 2.10 as 6 H singlet), three methoxyl groups (δ 3.36, 3.40, and 3.43 corresponding to 3 H singlets), and C-1, β-proton at δ 5.00 (quartet $J_1 + J_2$ = 14 Hz). The 1β,8β,14α-triacetyl compound was obtained as an oil. Its nmr spectrum shows an *N*-ethyl group (3 H triplet, J = 7 Hz) centered at δ 1.09, three acetoxyl groups (δ 2.05, 2.10, and 2.12 corresponding to 3 H singlets), three methoxyl groups (δ 3.36 corresponding to three protons and δ 3.40 corresponding to six protons), and a C-1 proton as a multiplet at δ 5.30.

It will be noted that the structure of neoline, as proposed by Wiesner, *et al.*,[2] corresponds to epimer **1,** while that proposed by Marion, *et al.*,[3] corresponds to epimer **4.** The epimer **1,** mp 159–160°, $[\alpha]^{26}D$ + 21° (*c* 4.0, ethanol) *is identical with natural neoline,* mp 161°[2], $[\alpha]^{26}D$ +22° (*c* 4.3, ethanol); thus a mixture of the two compounds produced a single spot in tlc and had an undepressed melting point (159°). The ir spectra, obtained in chloroform solution, KBr pellet, and Nujol mull, and the nmr spectra in $CDCl_3$ of both substances were respectively superimposable. Triol **1** and neoline also had identical ^{13}C nmr spectra. Thus neoline must be assigned structure **1** and the revised structure **4,** based on the reported correlation with chasmanine,[3] is in error.

The structures previously assigned to chasmanine[4,5] and homochasmanine[8] must now be considered. Chasmanine has been correlated[3] with neoline by treatment of each alkaloid with sodium hydride and methyl iodide in refluxing dioxan for 12 and 24 hr, respectively. The products, designated as 8,14-di-*O*-methylchasmanine and 1,8,14-tri-*O*-methylneoline, respectively, were shown to be identical by mixture melting point, rotation, behavior on tlc, infrared and nmr spectra, and by identical Debye–Scheerer diagrams. We have replicated this correlation, and there is no doubt about the identity of the two products. Consequently on the basis of the correlation of chasmanine with neoline, chasmanine must also have a 1α-substituent and accordingly be assigned structure **2.** A ^{13}C nmr study of chasmanine, delphonine, neoline, and delphisine when compared with published values[9] for lycoctonine and browniine confirms this assignment.[10] Because chasmanine diacetate has been converted to homochasmanine by treatment with methanol under pressure, followed by saponification, homochasmanine may be assigned structure **9.**

Because chasmanine, homochasmanine, and neoline have been related to delphisine, the absolute configuration of delphisine derived by X-ray analysis[6] applies to these compounds as well.

Acknowledgment. It is a pleasure to express thanks to Professors T. Okamoto and Léo Marion for reference samples of neoline, to Dr. O. E. Edwards for a sample of chasmanine, to Professor K. Wiesner for infrared spectra of neoline and certain of its derivatives, and to Mr. Courtney Pape for providing the ^{13}C nmr spectra.

References and Notes

(1) W. Freudenberg and E. F. Rogers, *J. Amer. Chem. Soc.*, **59**, 2572 (1937).
(2) K. Wiesner, H. W. Brewer, D. L. Simmons, D. R. Babin, F. Bickelhaupt, J. Kallos, and T. Bogri, *Tetrahedron Lett.*, 17 (1960).
(3) L. Marion, J. P. Boca, and J. Kallos, *Tetrahedron Suppl.*, **8**, Part I, 101 (1966).
(4) O. Achmatowicz, Jr., Y. Tsuda, L. Marion, T. Okamoto, M. Natsume, H. H. Chang, and K. Kajima, *Can. J. Chem.*, **43**, 825 (1965).
(5) O. E. Edwards, L. Fonzes, and L. Marion, *Can. J. Chem.*, **44**, 583 (1966).
(6) S. W. Pelletier, W. H. De Camp, S. Lajšić, Z. Djarmati, and A. H. Kapadi, *J. Amer. Chem. Soc.*, **96**, 7815 (1974).
(7) Combustion analyses for all new compounds were satisfactory.
(8) O. Achmatowicz, Jr., and L. Marion, *Can. J. Chem.*, **43**, 1093 (1965).
(9) A. J. Jones and M. H. Benn, *Can. J. Chem.*, **51**, 486 (1973). The structure shown in this paper for the base delphonine is incorrect. Wiesner, *et al.* (K. B. Birnbaum, K. Wiesner, E. W. K. Jay, and L. Jay, *Tetrahedron Lett.*, 867 (1971)), have demonstrated that the methoxyl group at C-1 in delphinine has an α-equatorial configuration (cis to the nitrogen bridge).
(10) S. W. Pelletier and Z. Djarmati, unpublished work.

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Organosilicon Iminamino Radicals from the Addition of Silyl Radicals to Diphenyldiazomethane

Sir:

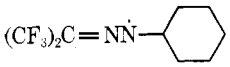
In an attempt to generate observable quantities of arylsilyl radicals *via* hydrogen abstraction by diphenylmethylene

$$Ph_2CN_2 \longrightarrow Ph_2C: + N_2$$

$$Ph_2C: + HSiRR'R'' \longrightarrow Ph_2CH\cdot + \cdot SiRR'R''$$

solutions of diphenyldiazomethane in liquid organosilanes[1] were irradiated with ultraviolet light directly in the microwave cavity of an electron spin resonance spectrometer.[2] Esr signals were obtained from all silanes examined, but the presence of large nitrogen splittings in the esr spectra immediately revealed that the radicals detected were *not* the desired silicon-centered radicals. Instead we had generated *N*-silyl derivatives of a new class of radicals, the iminamino radicals >C=N$\dot{N}$–, not previously detected by esr spectroscopy.

The iminamino radical



has been postulated as an intermediate in the chain-carrying steps in the thermal reaction of bis(trifluoromethyl)diazomethane and cyclohexane.[3] The addition of carbon-centered radicals to diazo compounds leading to the formation of other iminamino radicals has also been postulated.[4] The opportunity to present direct evidence for the process, the continued interest in the electronic structure of the isoelectronic iminoxy radicals >C=NO·,[5] and the scarcity of spectroscopic information about nitrogen-centered radicals with organometallic substituents[6] have together prompted this report.

Iminamino radicals have also been postulated to arise from lead tetraacetate oxidation of hydrazones,[7] but a nonradical pathway has also been suggested.[8] It is believed that other oxidizing agents do convert hydrazones to iminamino radicals.[9]

In Figure 1 is shown the esr spectrum, recorded under steady-state conditions at constant illumination, of a radical produced when trimethysilane was present in the reaction mixture.[10]

The iminamino structure was assigned to the radicals whose spectra were observed on the basis of the following spectral features: (1) The seven groups of peaks separated by *ca.* 10 G in the spectra from trimethylsilane and triphenylsilane are due to the interaction of the unpaired electron with two nonequivalent nitrogen atoms whose coupling constants (see Table I) are roughly in the ratio 1:2. (2) The additional group of peaks in the spectrum from diphenylsilane is due to interaction of the unpaired electron with a hydrogen atom whose coupling constant is of similar magnitude to that of one of the nonequivalent nitrogens. This additional splitting is assigned to the hydrogen attached to the silicon atom, an assignment confirmed by the reduction of this splitting when Ph_2SiD_2 was substituted for Ph_2SiH_2.[11] (3) Small splittings of *ca.* 1 G within the seven or eight groups of peaks are due to the further interaction of the unpaired electron with two hydrogen atoms. It was established that these hydrogens are in the ortho or meta positions of phenyl rings supplied by diphenyldiazomethane. The 1-G splittings vanished in experiments with diphenyldiazomethane-*d*[10] but persisted in experiments with *p,p'*-dimethoxydiphenyldiazomethane. By analogy with the iminoxy radical derived from benzophenone oxime, whose esr spectrum[5] resembles

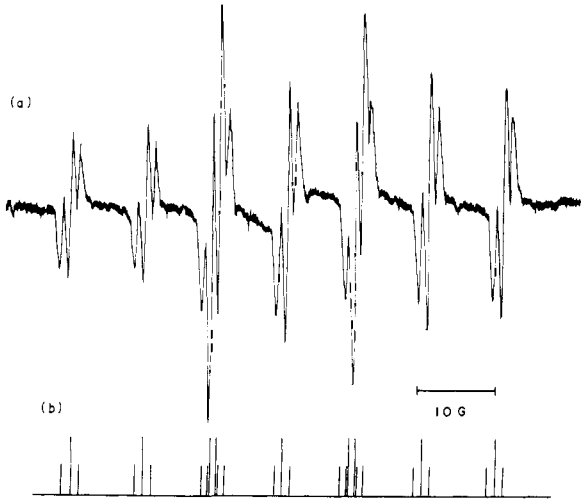
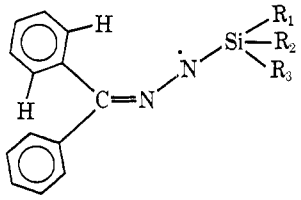


Figure 1. (a)Esr spectrum of $Ph_2C{=}N\dot{N}Si(CH_3)_3$, reaction mixture at room temperature; (b) reconstructed spectrum using coupling constants from Table I.

Table I. Hyperfine Coupling Constants (G) Deduced from Esr Spectra of Organosilicon Iminamino Radicals[a]



	a_{N_1}	a_{N_2}	a_{Ph-H}	a_{Si-H}
$R_1 = R_2 = R_3 = CH_3$	17.69	9.22	1.00	
$R_1 = H, R_2 = R_3 = Ph$	18.20	9.05	1.00	6.85
$R_1 = R_2 = R_3 = Ph$	18.35	8.72	0.95	
$R_1 = R_2 = R_3 = Et$	17.64	9.04	1.00	

[a] The uncertainty in the values reported is *ca.* 0.05 G.

those of the iminamino radicals reported here, these 1-G splittings are assigned to *two* of the hydrogens of one ring.

Additional support for the structure of the observed radicals and for a reaction mechanism including spin trapping of silyl radicals by diphenyldiazomethane comes from the nature of the reaction products and from the effects of radical scavenger on product yields.

The previously unknown trimethylsilylhydrazone of benzophenone[12] was isolated in 6% yield from the irradiation of diphenyldiazomethane in trimethylsilane.

$$Ph_2C{:} + HSi(CH_3)_3 \longrightarrow Ph_2CH\cdot + \cdot Si(CH_3)_3$$

$$(CH_3)_3Si\cdot + Ph_2CN_2 \longrightarrow (CH_3)_3Si\dot{N}N{=}CPh_2$$

$$(CH_3)_3Si\dot{N}N{=}CPh_2 + HSi(CH_3)_3 \longrightarrow (CH_3)_3SiNHN{=}CPh_2 + \cdot Si(CH_3)_3$$

The products $(CH_3)_3SiSi(CH_3)_3$, $(CH_3)_3SiCHPh_2$, and $Ph_2CHCHPh_2$ were also formed. The yields of $(CH_3)_3SiNHN{=}CPh_2$ and $(CH_3)_3SiSi(CH_3)_3$ dropped to zero when a radical scavenger, hydroquinone, was present in the reaction mixture. The yield of $(CH_3)_3SiCHPh_2$ dropped from 22 to 8% and that of $Ph_2CHCHPh_2$ from 30 to 10% in the presence of scavenger. The depression of yields by scavenger indicates that the products obtained in macroscopic yields are derived from free radicals whose lifetimes are sufficient to permit escape from the solvent cage in which the radicals are created. The rate of disappearance of diphenyldiazomethane is also reduced in the presence of scavenger, indicating that diphenyldiazomethane is involved in a chain process. These facts lend credence to the proposal that the silyliminamino radicals are formed by addition of a free silyl radical to the terminal nitrogen of the diazo compound.

It is not yet clear whether the products $(CH_3)_3SiCHPh_2$ and $Ph_2CHCHPh_2$ originate from coupling of trimethylsilyl and diphenylmethyl radicals, or whether instead radical addition to "the other end" of the diazo compound intervenes.

$$R\cdot + Ph_2CN_2 \longrightarrow RCPh_2N{=}N\cdot \xrightarrow{-N_2}$$

$$RCPh_2\cdot \xrightarrow[(CH_3)_3SiH]{} RCPh_2H \ (R = Ph_2CH, (CH_3)_3Si)$$

This reaction is suggested by the report that the esr spectrum of $Ph_2CHCPh_2\cdot$, and *not* of $Ph_2CH\cdot$, is observed when diphenyldiazomethane undergoes thermolysis in solvents containing easily abstractable hydrogen atoms.[13]

While the addition of silyl radicals to carbon-carbon π bonds is well-established[14,15] and forms the basis of many hydrosilylation reactions, additions of silyl radicals to other π bonds has generally been inferred from the diamagnetic

end products[16] rather than from direct observation of adduct radicals. McIntosh and Wan, however, observed the esr spectrum of $Ph_3SiOCPh_2\cdot$ formed by addition of the triphenylsilyl radical to the carbon-oxygen π bond of benzophenone.[17]

A full interpretation of the spectra we have observed in terms of details of radical structure awaits assignment of the nitrogen hyperfine coupling constants to the individual nonequivalent atoms and the resolution of the ^{29}Si coupling. That iminamino radicals resemble their iminoxy analogs[5] in being σ radicals with a C-N-N bond angle considerably less than 180° is already clearly indicated by the coupling between the unpaired electron and *two* nonpara hydrogens of carbon-bound phenyl groups.

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References and Notes

(1) Tetrahydrofuran or 1-methyltetrahydrofuran was added as solvent for solid triphenylsilane. Reaction mixtures were degassed and sealed.
(2) An Eimac R-150-2 xenon lamp was focused on a Pyrex sample tube in the microwave cavity of a Varian E-3 esr spectrometer. Most irradiations were carried out at room temperature.
(3) W. J. Middleton, D. M. Gale, and C. G. Krespan, *J. Amer. Chem. Soc.*, **90**, 6813 (1968).
(4) L. Horner and H. Schwarz, *Justus Liebigs Ann. Chem.*, **747**, 1 (1971).
(5) T.-S. Lin, private communication; B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966); R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).
(6) R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **95**, 7897 (1973).
(7) D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Amer. Chem. Soc.*, **83**, 747 (1961).
(8) M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone, *J. Chem. Soc. C*, 735 (1967).
(9) J. Buckingham, *Quart. Rev., Chem. Soc.*, **23**, 37 (1969); C. Wintner and J. Wiecko, *Tetrahedron Lett.*, 1595 (1969); R. B. Woodward and C. Wintner, *ibid.*, 2697 (1969); see earlier references contained in these papers. Wintner and Wiecko gave the name "hydrazonyl radicals" to the species $R_1R_2C{=}NNR_3$ but we consider "iminamino" to be more appropriate.
(10) These radicals have appreciable lifetimes. Pulsed photolysis experiments (*cf.* ref 15) indicated lifetimes to be *ca.* 0.1 sec at room temperature and >1 sec at −40°.
(11) We have not yet succeeded in resolving ^{29}Si coupling due to insufficient signal-to-noise ratio.
(12) An authentic sample was prepared by trimethylsilylation of benzophenone hydrazone. Satisfactory elemental analysis and spectroscopic properties were found.
(13) F. A. Neugebauer and W. R. Groh, *Tetrahedron Lett.*, 1005 (1973). These authors suggest that $Ph_2CHCHPh_2$ arises from dimerization of $Ph_2CH\cdot$ followed by loss of a hydrogen atom through abstraction by $Ph_2C{:}$. This seems less likely than the sequence suggested by us.
(14) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969).
(15) K. Y. Choo and P. P. Gaspar, *J. Amer. Chem. Soc.*, **96**, 1284 (1974).
(16) K. Kühlein, W. P. Neumann, and H. P. Becker, *Angew. Chem., Int. Ed. Engl.*, **6**, 876 (1967).
(17) A. R. McIntosh and J. K. S. Wan, *Can. J. Chem.*, **49**, 812 (1971).

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Catalysis of Peroxymonosulfate Reactions by Ketones

Sir:

The Baeyer-Villiger reaction of Caro's acid and ketones to produce esters is well known.[1] These reactions are usually conducted in acidic media. Hydrogen peroxide and acetone are also known to react in aqueous solution[2] and a variety of peroxides can be produced. In the course of a study of peroxymonosulfate ion (HSO_5^-) reactions in weakly alkaline solutions, it was observed that ketones catalyze a number of reactions in an unexpected manner.

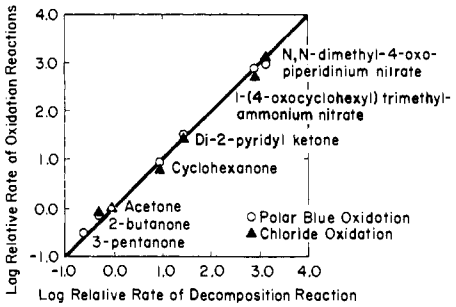

Figure 1. Linear free energy relationship for several ketones at pH 9.0.

Table I. Catalysis of Peroxymonosulfate Reactions by Ketones

Ketone	Relative Rates of Reactions[a]: Decomposition[b] of peroxymonosulfate	Chloride[c] Oxidation	Polar Blue[d] Oxidation
None	<0.1	<0.1	<0.1
Acetone	1.0	1.0	1.0
Cyclohexanone	9.4	6.1	8.8
N,N-Dimethyl-4-oxopiperidinium nitrate	1400	1300	930

[a] Each reaction was conducted at 2.7×10^{-3} *M* HSO_5^- and pH 9.0. The rates in the presence of acetone have arbitrarily been taken as 1.0. Other rates are normalized to that of acetone at 5.0×10^{-3} *M* (reactions are first-order in ketone). [b] Measured by iodometric titration. [c] The appearance of hypochlorite was followed spectrophotometrically at 292 mμ. Chloride ion concentration was 2.4×10^{-2} *M*. [d] The disappearance of dye was followed spectrophotometrically at 620 mμ. Dye concentration was 6.5×10^{-5} *M*.

We present here results obtained on the catalysis of three reactions: (1) the decomposition of the peroxide

$$2HSO_5^- \longrightarrow 2H^+ + 2SO_4^{2-} + O_2 \quad (1)$$

(2) the oxidation of chloride ion to hypochlorite ion

$$HSO_5^- + Cl^- \longrightarrow OCl^- + H^+ + SO_4^{2-} \quad (2)$$

and (3) the oxidation of Polar Brilliant Blue GAW (an anionic dye) for which the complete stoichiometry is as yet unknown. Table I illustrates this catalysis for these three reactions in the presence of three ketones.

The rates of all three reactions are enhanced by the presence of the ketones, and the heterocyclic ketone, *N,N*-dimethyl-4-oxopiperidinium nitrate (hereafter referred to as ketone I), is particularly effective. (This compound is so active that a much lower concentration must be used to obtain accurate rate measurements.) Another very active catalyst is 1-(4-oxocyclohexyl)trimethylammonium nitrate.

It is evident from Table I that there is a marked parallelism among the three reactions suggesting that a common intermediate is involved. The effect is further demonstrated for seven ketones in Figure 1. As can be seen, an excellent linear free energy relationship is obtained. Also, Table I and Figure 1 show that a variety of ketone structures can be employed as catalysts for these reactions.

Oxygen and hypochlorite production measurements clearly indicate the stoichiometry shown in eq 1 and 2. However, with certain ketones side reactions such as the Baeyer-Villiger oxidation of the ketone and chlorination of the ketone by hypochlorite ion[3] can complicate the overall reaction. For instance, with cyclohexanone a significant loss (15-30%) of ketone can be observed and only about 70% of