

from either analytical treatment. The value in Table III is obtained from the plot of eq 6.

Similar data for the reaction of benzyl cation with methanol, over a concentration range of 4–60 mM, show only a small degree of curvature and, when subjected to the foregoing treatment, give a value of $(6 \pm 1.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This is slightly lower than the previous value² of 7.4×10^7 , but not in disagreement. The value for benzyl cation and ethanol is taken from the previous paper² since the very small deviation from linearity did not seem to call for the more complex interpretation. The uncertainty in the values of k_m is approximately $\pm 20\%$, in $K_e k_d$ approximately $\pm 25\%$. The values for k_m indicate no obvious trend in the alcohol series.

The higher reactivity of the arylcarbenium ion toward alcohol dimer than toward monomer is interesting but may not be readily predictable on any simple basis involving either higher electron density on the oxygen in the dimer, or a lower charge repulsion toward the reacting carbonium ion. The product of the reaction is an ether,¹⁶ and it is interesting to note that the leaving group from the protonated ether intermediate formed from the monomer is a proton, while for that formed from the dimer is the alkoxonium ion, a bonded, stabilized state of the proton.

Acknowledgment. We have had several helpful discussions with colleagues in our Department, notably Professors Harold Shechter and Gideon Fraenkel. We are indebted to Dr. James Gavlas for his help in obtaining some of the rate constants for

the reactions with halide ions. Mr. Ed Ray has been responsible for the operation and maintenance of the Linac and the detection equipment.

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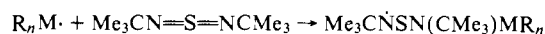
Radical Additions to Di-*tert*-butylsulfur Diimide and Di-*tert*-butylcarbodiimide¹

G. Brunton,² J. F. Taylor,³ and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9. Received November 21, 1975

Abstract: A variety of transient radicals, $R_nM\cdot$, add to di-*tert*-butylsulfur diimide to give a new class of nitrogen-centered radicals, *N*-aminothiyl-*N*-alkylamino radicals, $\text{Me}_3\text{CNSN}(\text{CMe}_3)\text{MR}_n$. The EPR parameters of these radicals indicate that the unpaired electron is located principally in the $N_\alpha 2p_z$ orbital and that the α -*tert*-butyl group, the two nitrogens, and the sulfur lie in, or close to, the nodal plane of this orbital. These radicals decay with first-order kinetics, and some of them are very persistent. Radical addition to di-*tert*-butylcarbodiimide appears to be a less facile process, since only $\text{CF}_3\text{O}\cdot$ gave a simple adduct, $\text{Me}_3\text{CN}=\text{C}(\text{OCF}_3)\text{NCMe}_3$. This 1,3-diazaallyl radical decays with second-order kinetics; $\log(k/\text{M}^{-1} \text{ s}^{-1}) = (7 \pm 1) - (2.5 \pm 1.2)/\theta$, where $\theta = 2.3RT$ kcal/mol. Trimethylsilyl radicals add to di-*tert*-butylcarbodiimide (and other carbodiimides), but only the extremely persistent $(\text{Me}_3\text{Si})_2\dot{\text{C}}\text{N}(\text{SiMe}_3)_2$ radical can be observed.

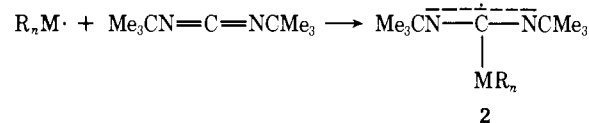
Very few nitrogen-centered radicals have been prepared by radical additions to a common precursor. More usually, N-centered radicals have been generated from precursors individually synthesized (often with considerable difficulty), such as tetrazenes,^{4,5} dialkylaminodialkoxophosphines,^{5,6} alkoxyalkylamines,^{7–9} etc., which has made studies of structural effects on EPR spectra and on reactivity slow and tedious. In a continuing search for simple methods for generating N-centered radicals, we found that certain readily prepared transient radicals, $R_nM\cdot$, will add to di-*tert*-butylsulfur diimide to give a new class of radicals, *N*-aminothiyl-*N*-alkylamino radicals (1).



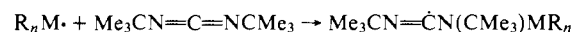
1

Radical additions to the structurally related di-*tert*-butyl-

carbodiimide were also explored, but only one member of the desired family of 1,3-diazaallyl radicals could be identified.



Iminoyl radicals,¹⁰ which would be formed by attack at one of the carbodiimide's nitrogen atoms, were never detected.



Experimental Section

Di-*tert*-butylsulfur diimide¹¹ and di-*tert*-butylcarbodiimide¹² were prepared by literature methods. All other materials were commercially available samples which were used without further purification. Transient radicals were generated in cyclopropane as solvent directly

Table I. Me₃CNSN(CMe₃)MR_n Radicals in Cyclopropane. EPR Parameters (hfs in gauss) and Rate Constants for Decay at 20 °C

R _n M	<i>g</i>	<i>a</i> ^{N_α}	<i>a</i> ^{N_γ}	<i>a</i> ^{other}	Δ <i>H</i> _{pp} ^a	<i>k</i> ^{20°, s⁻¹}
F ₃ C	2.0060	12.6	0.9 ^b	2.0 (3 × ¹⁹ F) ^b	1.4	4 × 10 ⁻³
Me ₃ Si	2.0064	12.0	<i>c</i>	8.3 ₄ (³³ S)	1.8	≤10 ⁻⁵
<i>n</i> -Bu ₃ Si	2.0064	12.0	<i>c</i>	8.3 ₄ (³³ S)	1.8	≤10 ⁻⁵
(EtO) ₂ P=O	2.0062	12.2 ₅	1.0	10.0 ₅ (³¹ P)	0.7	0.25
F ₃ CS	2.0054	12.4	<i>c</i>		2.4	0.30

^a Peak-to-peak line width. ^b Partly resolved. ^c Not resolved.

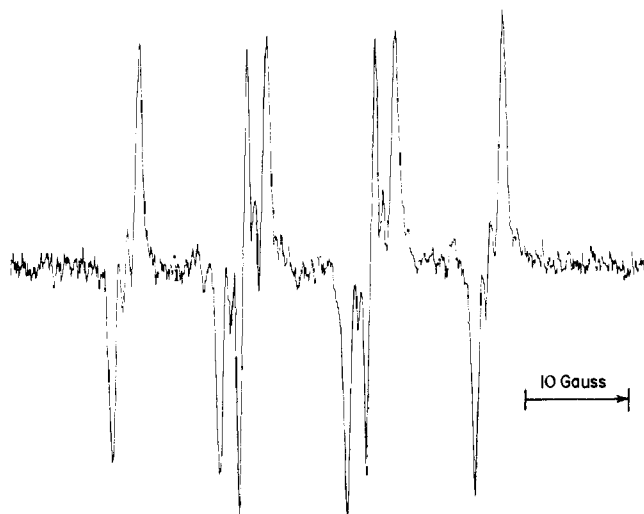


Figure 1. EPR spectrum of Me₃CNSN(CMe₃)P(=O)(OEt)₂ in cyclopropane at 20°.

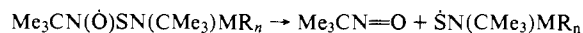
in the cavity of a Varian E-4 EPR spectrometer in the presence of the sulfur diimide or the carbodiimide. The following transients were produced using previously described photochemical methods:¹³ ·CH₃, ·CF₃, C₆H₅·, C₆F₅·, Me₃Si·, *n*-Bu₃Si·, Me₃Sn·, (EtO)₂P=O, F₃CO·, Me₃CO·, and F₃CS·. Radical decays were followed by the usual procedures.¹⁴

Results

EPR Spectra using the Sulfur Diimide. The principal feature in the EPR spectra of all **1** is the triplet due to N_α (*a*^{N_α} ~ 12 G). The lines are generally rather broad, and, since **1** having R_nM = (CH₃)₃Si and (CD₃)₃Si gave exactly identical spectra, the width of the lines is probably mainly a consequence of unresolved proton coupling from the α-*tert*-butyl group. The hyperfine splittings (hfs) are temperature independent (20 to -100 °C). The spectra do not saturate even at microwave power levels as high as 100 mW. The EPR parameters of those **1** that have, we believe, been unequivocally identified¹⁵ are given in Table I. The spectrum of **1** having R_nM = (EtO)₂P=O is shown in Figure 1.

Although the *g* values for **1** are in the range normally found in nitroxides^{16,17} and some **1** are very persistent, we are confident that the radicals observed are N-centered since they react rapidly with oxygen.¹⁹ This was shown by generating the very persistent Me₃CNSN(CMe₃)Si(*n*-Bu)₃ radical in di-*tert*-butyl peroxide at 20°, while a slow stream of argon was bubbled through the solution. When the light used to produce the *n*-Bu₃Si· radicals was cut off, the adduct radicals decayed extremely slowly unless the argon was replaced by air, in which case they were rapidly and completely destroyed and no new radicals were produced. A similar experiment with Me₃CNSN(CMe₃)(EtO)₂P=O gave the same result, but the short lifetime of this radical necessitated the continuous photoproduction of (EtO)₂P=O radicals. Our failure to detect nitroxides in these reactions is probably due to their rapid β scission to give nitrosoisobutane and the stabilized,²⁰ but dif-

ficult to detect,²¹ aminothiyl radicals,



Although **1** are structurally related to some recently reported dibenzenesulfenamidyl radicals,²² ArSNSAr, it is worth noting that the latter radicals do not react with oxygen, presumably because they are more stabilized than the **1** type of radical.

The persistence of the two trialkylsilyl adducts was so pronounced ($\tau_{1/2} \sim 1$ day, see below) as to suggest that they might not be formed by a single addition step. That is, in previous work²³⁻²⁵ we have shown that many radicals having *tert*-butyl substituents can have these substituents replaced by trialkylsilyl groups via a series of eliminations and additions, and that the resultant silylated radicals are more persistent than the initial radical. Such "secondary" radicals generally develop slowly after prolonged irradiation and this provides a method for distinguishing them from "primary" radicals.²⁶ In the present instance, when a fresh sample of sulfur diimide, Me₃SiH, and di-*tert*-butyl peroxide in cyclopropane was irradiated at low light intensity, the EPR signal we attribute to Me₃CNSN(CMe₃)SiMe₃ grew linearly with time (rather than at an accelerating rate) and, when the light was cut off, the signal decayed very slowly.²⁷ This radical is therefore a "primary" radical derived directly from the reactants. In fact, it would appear that the sulfur diimide (in contrast to the carbodiimide, see below) does not form "secondary" radicals very readily, since all the systems that gave identifiable **1** gave spectra that did not change even upon prolonged irradiation (up to 3 h for the (EtO)₂P=O adduct).

EPR Spectra Using the Carbodiimide. Only the CF₃O· radical gave a simple adduct with di-*tert*-butylcarbodiimide. The EPR parameters for the adduct (Table II) indicate that this radical is a 1,3-diazaallyl radical (**2**, R_nM = CF₃O) which has the unpaired electron distributed equally between the two nitrogen atoms. Only two radicals of this class have been reported previously.²⁸ They are structurally related to the present radical, but were generated by hydrogen abstraction from the appropriate amines. Their EPR parameters are included in Table II.

The CF₃O· radical did not add to dicyclohexylcarbodiimide nor to bis(trimethylsilyl)carbodiimide. No EPR signals could be observed at room temperature, and at low temperatures only the solvent derived cyclopropyl radical was seen.²⁹

No radicals could be detected during the initial stages of the reaction of Me₃Si· radicals with di-*tert*-butylcarbodiimide. However, after even a brief period of photolysis, the extremely persistent (Me₃Si)₂CN(SiMe₃)₂ radical was produced. We have generated this radical previously by Me₃Si· additions to a number of cyanoalkanes,²³ but much more intense spectra are obtained from the carbodiimide. By using (CD₃)₃Si· the line widths for the tetrasilylated adduct are reduced by about a factor of three and the resolution of the spectrum is greatly improved. This allows more accurate and more complete measurement of the EPR parameters, i.e., for [(CD₃)₃Si]₂CN[Si(CD₃)₃]₂ in cyclopropane at 20°, *g* = 2.0026, *a*^{14N} = 1.95, *a*^{29Si}(2Si) = 14.11, *a*^{29Si}(2Si) = 20.42, *a*^{13C}(6C) = 4.70, *a*^{13C}(1C) = 30.73 G. The (Me₃Si)₂CN(SiMe₃)₂ was also the

Table II. EPR Parameters (hfs in gauss) for Me₃CNC(MR_n)=NCMe₃ Radicals

R _n M	Solvent	Temp, °C	g	a ^N (2N)	a ^{other}	Ref
CF ₃ O	Cyclopropane	20	2.0052	8.75	0.30 ^a	This work
H	Isopentane	-70	2.0046	8.5	3.0 ^b	28
H ₃ C	Isopentane	-70	2.0050	8.6	2.5 ^b	28

^a Poorly resolved multiplet with >16 lines, presumably due to 18 H and 3 F. ^b a^H for R_nM group.

only radical detected during the reaction of Me₃Si· with dicyclohexyl and bis(trimethylsilyl)carbodiimides.

Decay Kinetics. All **1** are moderately persistent (particularly at low temperatures), presumably because N_α is sterically well protected and there is no hydrogen attached to a β atom.^{20,30} They decay with first-order kinetics and the rate constants for decay at 20° have been included in Table I. No decay process was examined in detail, since it seems likely that different **1** will decay by different mechanisms, e.g., loss of R_nM·, loss of Me₃C· from N_γ, attack upon the surrounding medium,⁵ etc.

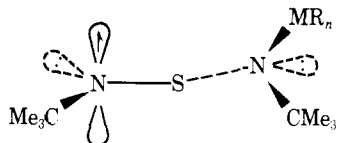
The diazaallyl radical **2**, R_nM = CF₃O, is appreciably more persistent than the two previously reported diazaallyls.²⁸ In the temperature range 10 to -50 °C decay occurs with very "clean" second-order kinetics and presumably yields the dimer. The rate constant for decay, *k* (= 2*k*_r), is ca. 5 × 10⁴ M⁻¹ s⁻¹ and shows only a slight variation with temperature that can be represented by

$$\log(k/M^{-1} s^{-1}) = (7 \pm 1) - (2.5 \pm 1.2)/\theta$$

where $\theta = 2.3RT$ kcal/mol.

Discussion

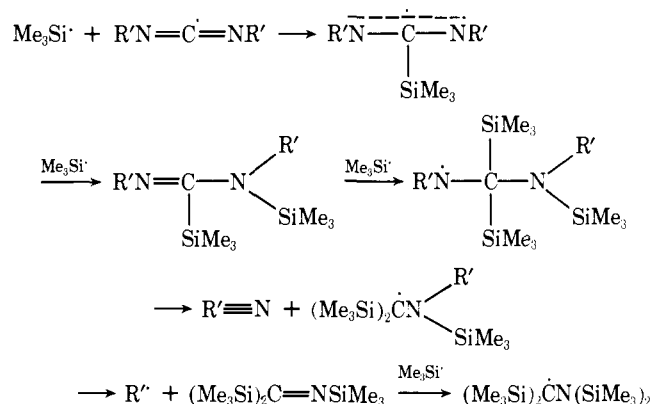
All **1** have N_α hfs of the magnitude expected for N-centered radicals having the unpaired electron located predominantly in the N_α 2p_z orbital.^{4,31} These radicals are structurally related to the *N*-alkoxy-*N*-alkylamino radicals, RONR', first reported by Danen et al.^{7,8} The N_α hfs for RONR' radicals are ca. 14 G and their *g* values are in the range 2.0047–2.0050.⁷⁻⁹ Substitution of sulfur for oxygen would be expected to decrease the N_α hfs (because of the greater ability of sulfur to delocalize an adjacent unpaired electron,³² i.e., $-\dot{N}-\ddot{S}- \leftrightarrow -\dot{N}-\dot{S}^+-$), and increase the *g* value (because of the greater spin-orbit coupling constant for sulfur.^{33,34} Both these phenomena are observed and **1** are therefore expected to have a conformation in which the α-*tert*-butyl group, the sulfur, and the second nitrogen are constrained to lie in, or close to, the nodal plane of the radical. That is, **1** should prefer the following conformation.



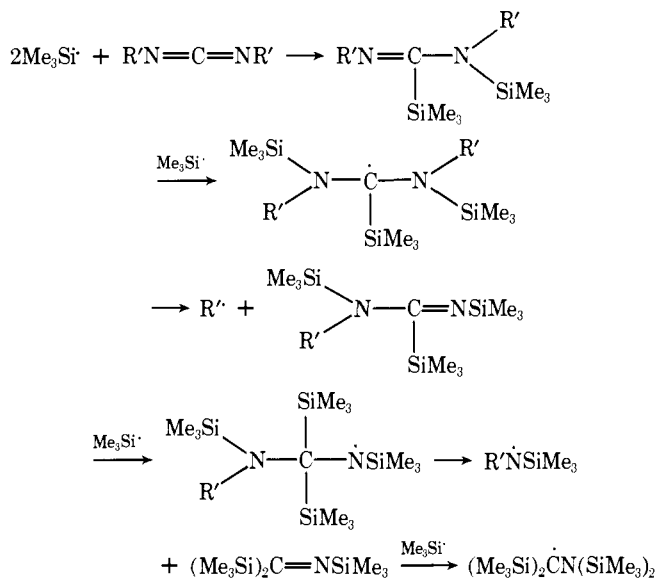
This conformation is supported by the small magnitude (ca. 1 G when resolved) of N_γ, which indicates that this nitrogen lies close to the nodal plane of the radical. Furthermore, the ³¹P hfs for the (EtO)₂P=O adduct (10 G) is relatively large for a δ-phosphorus,³⁶ which implies that this R_nM group lies well outside the radical's nodal plane. The other R_nM groups probably occupy similar positions, but their M hfs could not be resolved because ²⁹Si, ¹³C, and ³³S have smaller isotropic hyperfine coupling constants³⁸ and lower natural abundance than ³¹P. A further consequence of this conformation is that the ³³S_β hfs (found for **1** having R_nM = R₃Si) is probably of positive sign.

In their preferred conformation the radical centers in all **1** (i.e., N_α) are rather well protected by the adjacent Me₃C and SN(MR_n)CMe₃ groups. Since **1** are also stabilized radicals²⁰

Scheme I



Scheme II



(because of electron delocalization) it is not surprising that these radicals show no observable tendency to dimerize. Instead, decay occurs by first-order processes. The large variation in the rate constants for the first-order decays suggests that different **1** may decay by different routes. In fact, our failure to identify more radicals of this type may be due to the short lifetimes of certain **1** rather than to the absence of reaction between R_nM· and the sulfur diimide.

The carbodiimide appears to be even less reactive toward R_nM· radicals than the sulfur diimide. While it is possible that some R_nM· radicals add but do not give adducts sufficiently persistent to be observed, it is certain that CH₃ and (EtO)₂P=O do not add readily, since their EPR spectra can be seen in the presence of the carbodiimide. The lower radical trapping efficiency of the carbodiimide may be due to enthalpy effects. That is, the addition of R_nM· to the central carbon (or to a nitrogen) of the carbodiimide will probably be less exothermic than addition to the nitrogen of the sulfur diimide, since two π bonds are broken in the latter reaction.

1,3-Diazaallyl radicals must be planar radicals of the π -type since the two nitrogens are equivalent. Molecular models indicate that the radical centers in **2** ($R_1, R_2 = CF_3O$) are sterically somewhat less protected than the radical centers in all **1**. It is, therefore, not surprising²⁰ that although these radicals are stabilized they decay by a bimolecular radical-radical process, presumably a coupling reaction. The small preexponential factor for this reaction ($10^{7\pm 1} M^{-1} s^{-1}$) indicates that these radicals, like certain others,³⁹ dimerize slowly principally because of a high entropy of activation. That is, for these radicals the duration of an average encounter in solution is not sufficient to ensure that a configuration which would permit reaction is achieved, even though there is no real potential energy barrier to be crossed.

The mechanism by which $(Me_3Si)_2\dot{C}N(SiMe_3)_2$ is formed from $Me_3Si\cdot$ and carbodiimides cannot be unambiguously assigned, since no other radicals were detected during the initial stages of the reaction, even at temperatures as low as $-100^\circ C$. However, both for steric and energetic reasons the initial adduct is expected to be a diazaallyl and a possible overall reaction scheme is given in Scheme I. An alternative reaction scheme is shown in Scheme II.⁴⁰

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- NRCC Summer Student.
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Aminocyclopropyl Sulfoxides. Preparation and Reaction with Acids

Ronald H. Rynbrandt,* Fred E. Dutton, and Constance G. Chidester

Contribution from the Research Laboratories, The Upjohn Company, Kalamazoo, Michigan 49001. Received August 11, 1975

Abstract: The preparation and structural determination of the four isomeric aminocyclopropyl sulfoxides (1*RS*,2*SR*)-2-[(*SR*)-*p*-chlorophenyl)sulfinyl]-*N,N*,3,3-tetramethylcyclopropylamine (**2**), (1*RS*,2*SR*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N,N*,3,3-tetramethylcyclopropylamine (**3**), (1*RS*,2*RS*)-2-[(*SR*)-*p*-chlorophenyl)sulfinyl]-*N,N*,3,3-tetramethylcyclopropylamine (**4**), and (1*RS*,2*RS*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N,N*,3,3-tetramethylcyclopropylamine (**7**) are described. Reaction of **2** with various weak acids ($K_a < 10^{-4}$) in chloroform afforded 3-[(*p*-chlorophenyl)sulfinyl]-1-(*O*-substituted-hydroxy)-*N,N*,2,2-tetramethyl-1-propanamines (**8a-d**). Hydrolysis of **8a-d** afforded 2,2-dimethyl-3-[(*p*-chlorophenyl)sulfinyl]-propionaldehyde (**9**). Treatment of **2** with various strong acids ($K_a \geq 10^{-4}$) in chloroform afforded stereospecific (>90%) isomerization to **7**. These ring openings and isomerizations are rationalized in terms of zwitterionic intermediates.

We have previously described the preparation of aminocyclopropyl sulfides by the addition of thiocarbenes (or carbenoids) to enamines.²⁻⁴ Oxidation of these aminocyclopropyl sulfides with potassium permanganate in aqueous acetic acid afforded ring-opened sulfone acids and/or ketones.^{4,5} It was proposed that these ring openings occurred via aminocyclo-

propyl sulfone intermediates.⁵ We have subsequently prepared an aminocyclopropyl sulfone and have shown that it undergoes a facile hydrolytic ring-opening reaction presumably via a zwitterionic intermediate.⁴ This paper describes the preparation of four isomeric aminocyclopropyl sulfoxides and their reactions with weak and strong acids.