an asymmetric conformer can optimize one hydrogen bond in a β turn at the expense of the other and still maintain undistorted backbone angles. This is the case for *cyclo*-(Gly-L-Pro-D-Ala)$_2$. The intermolecular hydrogen bonds seem to support the effect. The stronger one reinforces the peptide twist away from a possibly favorable 1N-H ··· 4O interaction and the weaker one reinforces the twist toward the existing favorable 4N-H ··· 1O hydrogen bond.

We take this opportunity to correct ϕ_1 from 109° to $-109°$ in the study[16] of the naturally occurring cyclic peptide, β-amanitin.

Acknowledgment. We wish to thank Drs. Lila Pease of Amherst College, C.-H. Niu of the National Institutes of Health, and Elkan Blout of the Harvard Medical School for providing the title compound and making the NMR data available to us. We acknowledge support of this research by the National Institutes of Health (GM 06920) and the National Science Foundation (CHE-7719899). This research was sponsored in part by the Energy Research and Development Administration under contract with Union Carbide Corp.

Supplementary Material Available: Temperature factors (1 page). Ordering information is given on any current masthead page.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 33. Diazirinyl Radicals[1]

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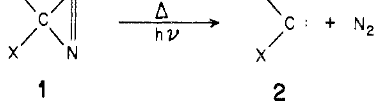
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa K1A OR6, Ontario, Canada. *Received July 28, 1978*

Abstract: Some 3-substituted diazirinyl radicals, $\overline{\mathrm{RC{=}NN}}\cdot$, have been generated by photolysis of the parent bromides in the presence of hexa-*n*-butylditin. The principal EPR parameters for 3-alkyldiazirinyl and 3-phenyldiazirinyl are similar: $a^{\mathrm{N}}(2\mathrm{N}) = 7.8$ G, $g = 2.0042$. INDO calculations give ^{14}N and ^{13}C hyperfine splittings in good agreement with experiment. Diazirinyls are II radicals, the two nitrogens' 2p$_z$ atomic orbitals making the major contribution to the semioccupied orbital. Diazirinyls decay with second-order kinetics to yield the corresponding nitrile. Like other N-centered three-membered ring radicals, they do not form nitroxides. Studies on the products of reaction of aziridinyl, $\overline{\mathrm{CH_2CH_2N}}\cdot$, with *tert*-butylperoxy have revealed that a nitroxide is probably formed, but it decomposes (to ethylene and NO) too rapidly for it to be detected. It is suggested that analogous processes occur with diazirinyls and other N-centered three-membered ring radicals.

The thermal[3-7] and photolytic[8-13] decomposition of 3-alkyl-3-halodiazirines and 3-aryl-3-halodiazirines, **1**,[14] have been studied as sources of "free" halocarbenes, **2**. The possibility that free radicals are involved in some of the systems investigated does not appear to have been explored, nor even suggested. We have discovered that 3-organodiazirinyl radicals, **3**, can be derived from a variety of **1**. These species represent a hitherto unidentified class of nitrogen-containing radicals. In this paper we report on their generation, identification by EPR spectroscopy, decay kinetics, and decay products.



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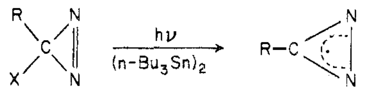

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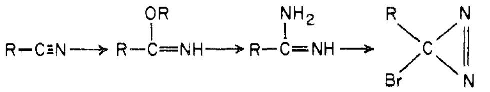
Experimental Section

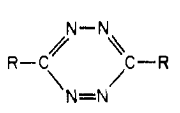
Materials. Bromodiazirines. The 3-alkyl-3-bromodiazirines and 3-phenyl-3-bromodiazirine were prepared from the corresponding amidine hydrochlorides by oxidation with freshly prepared aqueous sodium hypobromite in Me$_2$SO according to the general method described by Graham.[14] The volatile alkylbromodiazirines (R = CH$_3$ and CH$_3$CH$_2$) were collected continuously by means of a vacuum pump which pulled them through a train of four U-tubes held at -35, -80, and -80 °C with the gases bubbling through *n*-pentane, and -196 °C. These diazirines were retained in the pentane-filled U-tube. The less volatile organobromodiazirines (R = (CH$_3$)$_3$C, C$_6$H$_5$, and C$_6$H$_5$CH$_2$) were extracted continuously into *n*-pentane and were then purified by column chromatography through silica gel. The infrared



spectra of the bromodiazirines were in good agreement with the literature.[14,15]

3-Benzyl-3-bromo-[3-^{13}C]diazirine was prepared from $C_6H_5CH_2{}^{13}CN$ (90 atom % ^{13}C, Merck Sharp and Dohme) by Graham's method.[14]

Tetrazines, 4. These compounds were synthesized because they were potential products from the bimolecular self-reaction of diazirinyl radicals (vide infra). 3,6-Dimethyltetrazine and 3,6-diphenyltetrazine were prepared by the method of Curtius et al.[16] from the corresponding dihydrotetrazines, **5,** themselves prepared[16] from hydrazine and the appropriate nitrile. The physical characteristics of both tetrazines and both dihydrotetrazines agreed with the literature data.[16]



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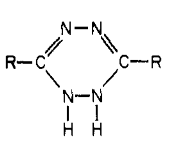

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R = CH_3, C_6H_5

Product Studies. The Self-Reaction. Thermolysis of 3-methyl-3-bromodiazirine at 60 °C in the presence of hexa-*n*-butylditin (both neat and in pentane as solvent) gave vinyl bromide as the major, and only identified, product. It is clear that diazirinyl radicals are not produced and that the vinyl bromide is formed from the bromocarbene.[3-13]

$$CH_3CBrN_2 \xrightarrow{\Delta} N_2 + CH_3CBr \rightarrow CH_2{=}CHBr$$

Similar experiments with 3-benzyl-3-bromodiazirine yielded β-bromostyrene as the only identifiable product.

UV photolysis of a pentane solution of 3-methyl-3-bromodiazirine and the ditin at −70 °C also gave vinyl bromide as the major, and only identifiable, product. 3-Benzyl-3-bromodiazirine again yielded only β-bromostyrene under these conditions. These results imply that formation of diazirinyl radicals is *not* the major reaction occurring in the EPR spectrometer.

In neither the thermal reaction nor in the photoreactions was there any trace of the anticipated tetrazine, **4.** Separate experiments showed that the tetrazines were reasonably stable thermally though they were unstable toward photolysis.[17] However, even under the photolytic conditions they would have survived in sufficient quantity to be identified if they had been formed to any significant extent.

Successful identification of the product of the bimolecular self-reaction of 3-substituted diazirinyl radicals was achieved by generating the diazirinyl radical thermally by the following route:

$$(CH_3)_3CONNOC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO\cdot + N_2$$

$$(CH_3)_3CO\cdot + (CH_3CH_2)_3SiH \rightarrow (CH_3)_3COH + (CH_3CH_2)_3Si\cdot$$

$$(CH_3CH_2)_3Si\cdot + RCBrN_2 \rightarrow (CH_3CH_2)_3SiBr + RCN_2\cdot$$

For example, 100 mg (4.7×10^{-4} mol) of 3-benzyl-3-bromodiazirine, 55 mg (4.7×10^{-4} mol) of triethylsilane, and 41 mg (2.4×10^{-4} mol) of *tert*-butyl hyponitrite in 1.7 mL of *n*-pentane were degassed and heated under nitrogen at 50 °C. The *only* products from the diazirine were β-bromostyrene and phenylacetonitrile. Their concentrations were monitored by VPC. Yields (× 10^4 mol) for diazirine, β-bromostyrene, and phenylacetonitrile were 2.4, 1.3, and 0.9, respectively, after 5 h; 1.3, 2.1, and 1.1 after 10 h; and 1.0, 2.3, and 1.2 after 15 h. The β-bromostyrene must arise from the carbene and the phenylacetonitrile from the diazirinyl radical

$$2C_6H_5CH_2CN_2\cdot \rightarrow 2C_6H_5CH_2CN + N_2$$

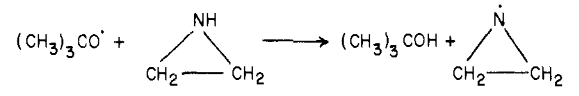
Reaction of the Aziridinal Radical with Oxygen. Most classes of nitrogen-centered radicals[18] react readily with molecular oxygen and with hydroperoxides to yield the corresponding nitroxides. Diazirinyl radicals, like other nitrogen-centered three-membered ring radicals, are interesting exceptions to this general rule (vide infra). Since no explanation for the unusual behavior of this class of radicals has ever been advanced we chose to examine the reaction of the simplest such radical with *tert*-butylperoxy radicals.

The aziridinyl radical, **6,** was produced by hydrogen atom abstraction from aziridine with photogenerated *tert*-butoxy radicals as originally described by Danen and Kensler.[23,24] The lines in the EPR spectrum of **6** were broadened in the presence of oxygen or *tert*-butyl hydroperoxide (a convenient source of *tert*-butylperoxy radicals) and the signal intensity decreased. However, there was no sign of the unknown[25] aziridinoxyl radical, **7.** Photolysis of 200 μL of aziridine, 100 μL of di-*tert*-butyl peroxide, and 50 μL of *tert*-butyl hydroperoxide in 100 μL of C_6D_6 for 30 min gave ethylene (identified by NMR and VPC) as the only organic product from the aziridine. Ethylene was *not* produced if the hydroperoxide was not present, provided that the solution was degassed and the photolysis carried out in the absence of oxygen. Nor was ethylene formed in the absence of aziridine. It seems clear that the aziridinoxyl radical is formed but rapidly loses nitric oxide.

Table I. EPR Parameters for 3-Substituted Diazirinyl Radicals[a] (Hyperfine Splittings in Gauss)

radical	g	a^N(2N)	a^H (n)[b]	$a^{^{13}C_\alpha}$
$CH_3CN_2\cdot$	2.004 21	7.77	2.78 (3)	*c*
$CH_3CH_2CN_2\cdot$	2.004 20	7.78	2.98 (2)	*c*
$(CH_3)_3CCN_2\cdot$[d]	2.004 16	7.75	*c*	*c*
$C_6H_5CN_2\cdot$[e]	2.004 18	7.84	*c*	*c*
$C_6H_5CH_2CN_2\cdot$[e]	2.004 20	7.82	2.95 (2)	12.4[f]

[a] In pentane at −80 °C unless otherwise specified. [b] n = number of equivalent H. [c] Not resolved. [d] A persistent radical with ≥13 lines was also produced on prolonged photolysis. [e] In toluene. [f] Using ^{13}C-enriched material.



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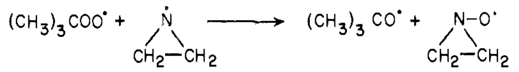

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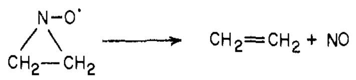


EPR Spectroscopic Studies. The diazirinyl radicals were generated directly in the cavity of a Varian E-4 EPR spectrometer by UV photolysis of degassed hydrocarbon solutions of the bromodiazirine and hexa-*n*-butylditin. The strongest spectra were obtained with ca. 0.3 M of the bromodiazirine and ca. 0.1 M ditin at low temperatures. However, the EPR parameters were independent of temperature in the range examined, viz., −90 to 0 °C. The kinetics of radical decay were followed in the usual manner.[26]

Results

EPR Spectra. The EPR parameters for the 3-substituted diazirinyl radicals prepared in this work are listed in Table I and the spectrum of 3-ethyldiazirinyl is shown in Figure 1. All the spectra are dominated by a 1:2:3:2:1 hyperfine splitting pattern due to two equivalent ^{14}N atoms, a^N = 7.8 G. For the methyl-, ethyl-, and benzyldiazirinyls, there is a further splitting due to the hydrogens on the carbon attached to the ring, $a^H \sim$ 2.8–3.0 G. Splittings by more remote protons could not be resolved. These hyperfine splittings prove that the observed radicals have retained the diazirine ring, while the relatively high g values (2.0042) imply that most of the unpaired spin density resides on the two nitrogen atoms (vide infra).

INDO Molecular Orbital Calculations. The $HCN_2\cdot$ and $CH_3CN_2\cdot$ radicals were studied by INDO calculations using standard procedures.[27,28] That is, all bond lengths and angles were varied in order to find the geometry that yielded the lowest total energy for each radical. The equilibrium geometries for $HCN_2\cdot$, **8,** and $CH_3CN_2\cdot$, **9,** indicate that the atom attached to the ring carbon is coplanar with the ring. The relative spin densities, the hyperfine splittings, and the total

Table II. Selected Results of INDO Calculations on $HCN_2\cdot$ with Optimized Geometry (Total Energy = −806.399 eV)

atom	rel spin densities s	p_x	p_y	p_z	hyperfine splitting, G
N (×2)	0.0193	−0.0141	0.0203	0.6206	7.3
C	−0.0190	−0.0311	−0.0112	−0.2411	−15.6
H	0.0101				5.5

Total Atomic Bond Indices N-N	C-N	H-C
0.9629	1.3938	0.9616

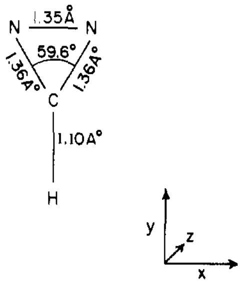
Table III. Selected Results of INDO Calculations on $CH_3CN_2\cdot$ with Optimized Geometry (Total Energy = −1037.255 eV)

atom	rel spin densities s	p_x	p_y	p_z	hyperfine splitting, G
N (×2)	0.0191	−0.0140	0.0197	0.6196	7.3
C_α	−0.0151	−0.0289	−0.0101	−0.2125	−12.4
C_β	0.0048	0.0061	0.0085	0.0164	3.9
H′ (×2)	−0.0119				−6.4
H″	−0.0345				−18.6
H (av)					−10.5

Total Atomic Bond Indices N-N	C-N	C-C	C-H′	C-H″
0.9596	1.3389	1.1020	0.9591	0.9493

Table IV. Rate Constants ($M^{-1}\ s^{-1}$) for Decay of Some Diaziridinyl Radicals at −75 °C

radical	solvent	$k^2_{EPR} \times 10^{-8}$
$CH_3CN_2\cdot$	pentane	4.8
$CH_3CH_2CN_2\cdot$	pentane	6.6
$C_6H_5CN_2\cdot$	toluene	2.0



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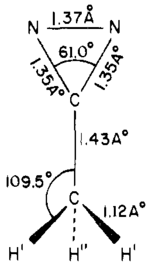

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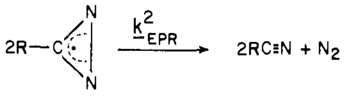
atomic bond orbitals obtained by these calculations are given in Tables II and III.

Decay Kinetics. Under steady photolysis the concentrations of all $RCN_2\cdot$ radicals were proportional to the square root of the incident light intensity. This indicates that diazirinyl radicals decay with second-order kinetics. Rate constants for the bimolecular decay of methyl-, ethyl-, and phenyldiazirinyl radicals, k^2_{EPR}, were measured by kinetic EPR spectroscopy[26] at −75 °C (see Table IV). Decay occurred with second-order kinetics in each case and at rates which approached the diffusion-controlled limit. The only products of this reaction are the corresponding nitrile (see Experimental Section) and, presumably, nitrogen.



$$2R{-}C\overset{N}{\underset{N}{\Big|}} \xrightarrow{k^2_{EPR}} 2RC{\equiv}N + N_2$$

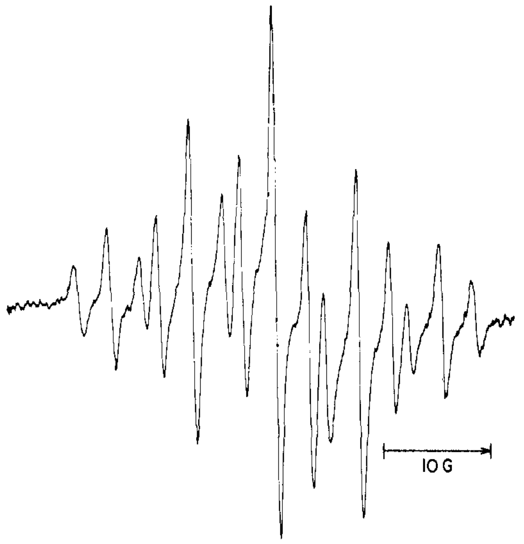
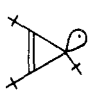


Figure 1. EPR spectrum of $CH_3CH_2CN_2\cdot$ in pentane at −75 °C.

Attempted Formation of Diaziridinoxyl. Generation of diaziridinyl radicals in the presence of oxygen or *tert*-butyl hydroperoxide does not yield a nitroxide which can be observed by EPR spectroscopy. However, the lines in the diaziridinyl spectrum are somewhat broadened and are reduced in intensity.

Discussion

The near identity in the a^N values for all the diazirinyl radicals indicates that their electronic structure is unaffected by the nature of the 3 substituent, *even when the substituent is phenyl.* This contrasts with the behavior observed with cyclopropenyl radicals—which are isoelectronic with the diazirinyls. Thus, for the tri-*tert*-butylcyclopropenyl radical, **10,** three equivalent σ structures are in rapid equilibrium.[29] However, replacement of one *tert*-butyl group by the 3,5-di-*tert*-butylphenyl group forces the pyramidal carbon into planarity to produce the Π radical, **11.**[30-33]



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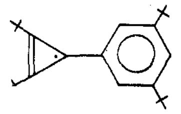

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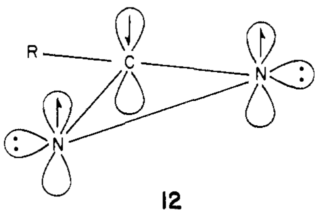
There is excellent agreement between the experimental a^N value for $CH_3CN_2\cdot$ (7.77 G) and the INDO calculated value (7.3 G). However, the measured (2.78 G) and calculated (10.5 G) a^H values are in rather poor agreement. The $C_6H_5CH_2{}^{13}CN_2\cdot$ radical was prepared so as to provide another check between experiment and theory. The value of $a^{^{13}C_\alpha}$ found for this radical (12.4 G) was in exact agreement with the INDO prediction. It should be noted that the INDO calculations indicate that the spin density on C_α is of negative sign and that the major contribution to the orbital occupied by the unpaired electron is made by the two nitrogens' $2p_z$ atomic orbitals, i.e., **12.** Or, in valence bond terms, diazirinyl radicals



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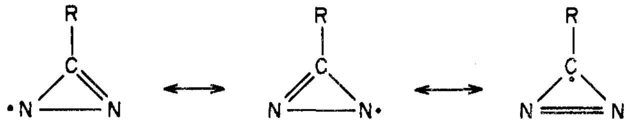
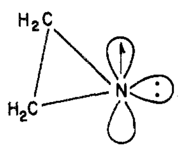
should be represented by **12a** and **12b** and not by **12c.** These canonical structures receive support from the INDO calculated



12a 12b 12c

bond indices which show partial double bond character in the C–N bonds and none in the N–N bond. Diazirinyl radicals are therefore similar to aziridinyl, **6**,[23,24] diaziridinyl, **13**,[34] and oxaziridinyl radicals, **14**.[35] All of these radicals are of the Π type.



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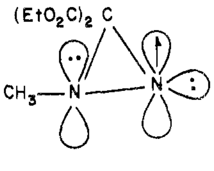

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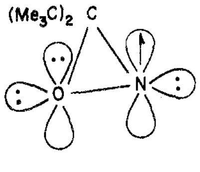

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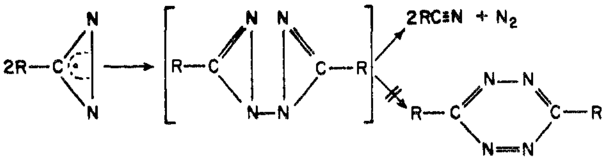
	6	13	14
a^N(G)	12.5	11.2, 18.7	12.1
a^H(G)	30.7 (4H)	2.6 (3H)	
g	2.0043	2.0039	2.0041

The bimolecular self-reaction of diazirinyl radicals yields the corresponding nitrile presumably via an initial head to head coupling. Tetrazine is not produced.



Diazirinyl radicals, like other nitrogen-centered three-membered ring radicals including aziridinyl,[23] diaziridinyl,[34] and oxaziridinyl,[35,36] do not form nitroxides.[37] This does not necessarily imply that diazirinyl radicals do not react with oxygen or peroxy radicals. As we have shown (see Experimental Section), the aziridinyl radical reacts readily with peroxy radicals but the nitroxide decomposes to yield ethylene and, presumably, nitric oxide so rapidly that the nitroxide cannot be detected. We suggest that an analogous reaction, leading to RCN and NO, occurs when diazirinyl radicals are generated in the presence of oxygen or peroxy radicals. However, we did not undertake product studies on this potential reaction because nitrile is also formed by the bimolecular self-reaction of diazirinyl radicals. Similar processes are expected to occur with **13** and **14**.

Acknowledgment. We would like to thank Mr. Stephen Rolfe for carrying out the INDO calculations.

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