Tetrazolinyl Radicals[1]

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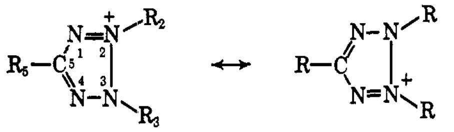
Received February 12, 1968

The electron spin resonance spectra of tetrazolinyl radicals are clarified and the structure is unequivocally assigned as cyclic.

We have previously reported the formation of a quite stable radical (not destroyed by oxygen) by the oxidation of formazans (RN=NCR=NNHR), by reduction of tetrazolium salts **1**, or by disproportionation of a mixture of the two.[2] We now present further evidence in support of the cyclic tetrazolinyl structure **2** for this radical. In **2** one might expect to find that all four nitrogen atoms have appreciable spin density since for the verdazyl radicals (**3**) the four nitrogen atoms are found to be nearly equivalent by esr spectroscopy.[3] Both **2** and **3** contain seven π electrons. On the other hand the open-chain structure isomeric with **2** contains only five π electrons. Moreover, it is obvious that for this structure (**4**) the spin should be concentrated on the terminal nitrogen atoms.



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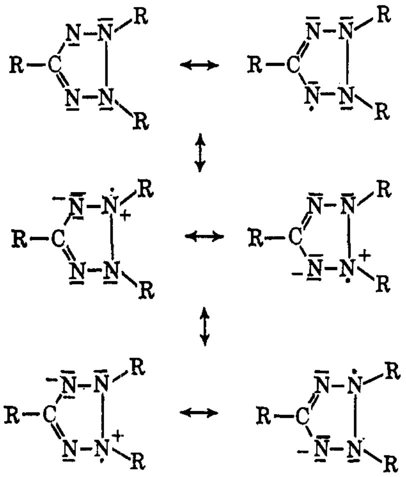

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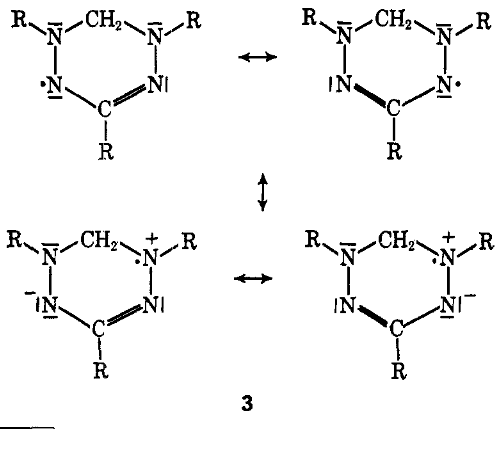

3

$$\mathrm{RN{=}NCR{=}N\dot{N}R \leftrightarrow RN{=}N\dot{C}RN{=}NR \leftrightarrow R\dot{N}N{=}CRN{=}NR}$$

4

The previously reported spectra for the tetrazolinyl radicals in dimethyl sulfoxide solution were poorly resolved. The spectra showed nine broad lines separated by 6-7 G, a pattern consistent with four nearly equivalent nitrogen atoms. We have now obtained much better resolved spectra in benzene solution by abstraction of a hydrogen atom from the formazan by di(*p*-tolyl)nitrogen.[4,5] Figure 1 gives *ca.* one-half of the esr spectrum of 2,3-diphenyl-5-carbethoxytetrazolinyl radical thus formed. This spectrum demands a^N = 8.00, 8.00, 5.55, 5.55 G and a^H = 1.0 (six hydrogens) and 0.5 G (four hydrogens). Figure 2 gives the spectrum for 2,3-bis(3,5-dichlorophenyl)-5-carbethoxytetrazolinyl radical. This spectrum requires a^N = 7.5, 7.5, 5.7, 5.7 G and a^H = 0.86 (six hydrogens) G. See Figure 3 for the esr spectrum of 2,3-diphenyl-5-carbethoxytetrazolinyl radical substituted with ^{15}N at N-1 and N-4. The spectrum now requires $a^{^{14}N}$ = 8.0, 8.0; $a^{^{15}N}$ = 7.6, 7.6; a^H = 1.0 (six hydrogens) and 0.5 (four hydrogens) G. For 2,3-bis(3,5-dichlorophenyl)-5-carbethoxytetrazolinyl radical substituted with ^{15}N at N-1 and N-4, nitrogen splittings of 8.1 (^{15}N) and 7.5 (^{14}N) G were observed. The largest value of $a^{^{14}N}$ in both of the tetrazoylinyl radicals is found to be at N-2 and N-3. However, the value of a^N at N-1 and N-4 is appreciable. Substitution of ^{15}N ($I = {}^1/_2$) for ^{14}N ($I = 1$) causes an increase in a^N of 1.4 ± 0.03 fold (the gyromagnetic ratio of ^{15}N/^{14}N is 1.40).

Hyperfine splitting constants for these and other radicals are summarized in Table I.

McLachlan molecular orbital calculations have been performed for structures **5** and **6** as a final verification of our structural assignment. We have used the same parameters employed in calculations of the verdazyls.[6]

$$\beta_{N_bN_c} = \beta_{CC},\ \alpha_N = \alpha_C + 1.2\beta_{CC};\ \beta_{C_aN_b} = 1.2\,\beta_{CC};\ \beta_{N_cC_d} = \beta_{CC}$$

The results are summarized in Table II and compared with spin densities (ρ) calculated from the experimental hyperfine splitting constants by use of the McConnell equation $a^H = -23.7\rho^C$ and the Stone and Maki equation $a^N = 28.6\rho^N$.[7]

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[1] This work was supported by a grant from the National Science Foundation (GP-6402X).

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TABLE I

HYPERFINE SPLITTING CONSTANTS OF TETRAZOLINYL RADICALS IN BENZENE SOLUTION

$R_2 = R_3$	R_5	$a_{1,4}{}^{14N}$	Registry No.	$a_{1,4}{}^{15N}$	Registry No.	$a_{2,3}{}^{N}$	a^{H}	g
C_6H_5	$C_2H_5O_2C$	5.55	16626-61-2	7.6	16626-68-9	8.00	1.0 (6), 0.5 (4)	2.0037
C_6H_5	$(CH_3)_3CO_2C$	5.50	16626-62-3	...		7.95	0.9 (6), 0.45 (4)	2.0037
3,5-$Cl_2C_6H_3$	$C_2H_5O_2C$	5.70	16626-63-4	8.1	16659-92-0	7.50	0.9 (6)	2.0038
4-$CH_3OC_6H_4$	$C_2H_5O_2C$	5.45	16626-64-5	...		8.65	1.0 (4), 0.5 (4)	
4-$C_2H_5O_2CC_6H_4$	$C_2H_5O_2C$	5.40	16626-65-6	...		7.25	0.95 (4), 0.5 (4)	2.0038
4-$NO_2C_6H_4$	$C_2H_5O_2C$	5.45	16626-66-7	...		6.65	Not assigned	
C_6H_5	C_6H_5	5.6	16626-67-8	8.0	16626-69-0	7.5	Not resolved	2.0037

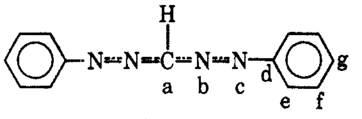
TABLE II

CALCULATED SPIN DENSITIES FOR 2,3-DIPHENYLTETRAZOLINYL RADICAL

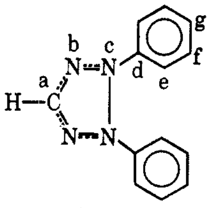
Position	Experimental[a] a, G	$\lvert\rho_\pi\rvert$	Calcd ρ_π (for **5**)	ρ_π (for **6**)	ρ_π (for **6a**)	ρ_π (for **6b**)
a	...	...	0.1264	−0.0609	−0.0521	−0.0374
b	5.5	0.19	−0.0505	0.2275	0.1720	0.1016
c	8.0	0.28	0.2420	0.2271	0.2477	0.2464
d	...	...	0.0159	−0.0352	−0.0331	−0.0169
e	1.0	0.042	0.0905	0.0568	0.0660	0.0797
f	0.5	0.021	−0.0297	−0.0252	−0.0264	−0.0283
g	1.0	0.042	0.1080	0.0482	0.0693	0.0848

[a] For 2,3-diphenyl-5-carbethoxytetrazolinyl radical.

The data of Table II support the assignment of structure as **6** rather than **5**. This is also consistent



5, 17 π electrons



6, 19 π electrons, $\beta_{N_cN_c} = 0$

6a, 19 π electrons, $\beta_{N_cN_c} = 0.4\beta_{CC}$

6b, 19 π electrons, $\beta_{N_cN_c} = 1.0\beta_{CC}$

with the lack of an effect of the substituent R_5 upon $a_{1,4}{}^{N}$ (see Table I), since for **5** $\rho_{C\text{-}5}$ is large, but for **6** $\rho_{C\text{-}5}$ is small. On the other hand $a_{2,3}{}^{N}$ is affected by the substituent on N-2 and N-3. The value of $a_{2,3}{}^{N}$ varies from 8.65 G with R = *p*-anisyl to 8.0 with R = phenyl, 7.50 with R = 3,5-dichlorophenyl, 7.25 with R = *p*-carbethoxyphenyl, and 6.65 with R = *p*-nitrophenyl. Here again we encounter an example wherein spin density is correlated by the Hammett σ constant.[8]

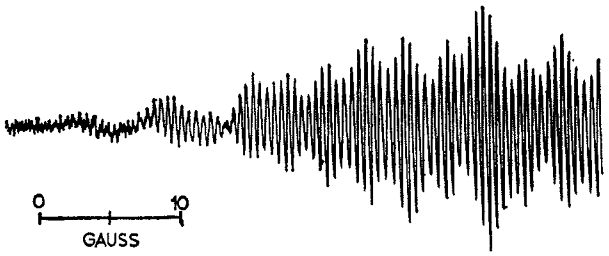


Figure 1.—Slightly more than one-half of the first derivative esr spectrum of 2,3-diphenyl-5-carbethoxytetrazolinyl radical in benzene solution.

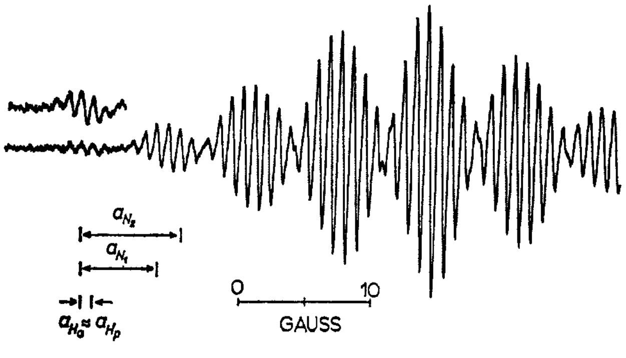


Figure 2.—Slightly more than one-half of the first derivative esr spectrum of 2,3-bis[3,5-dichlorophenyl]-5-carbethoxytetrazolinyl radical in benzene solution.

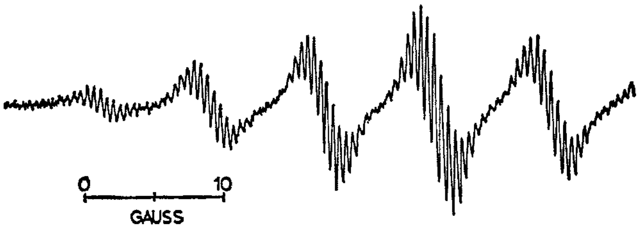
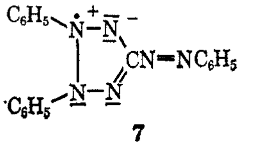


Figure 3.—Slightly more than one-half of the first derivative esr spectrum of 2,3-diphenyl-5-carbethoxytetrazolinyl radical substituted with ^{14}N at positions 1 and 4.

In the calculations summarized in Table II all the heavy atoms in **5** and **6** were assumed to be sp^2 hybridized since these compounds are hydrazyl derivatives. In diphenylpicrylhydrazyl the nitrogen atoms have bond angles of ~120°, consistent with sp^2 hybridization.[9] It is possible to conceive of electronic configurations, or equilibria between electronic configurations, for an acyclic radical derived from the tetrazolium salt which would predict appreciable spin density at all four nitrogen atoms (for example, with 19 π electrons). However, these configurations do not appear to be ground-state configurations. Moreover, the observation that *only* four nitrogen atoms show appreciable hyperfine splittting in the esr spectrum of **7** derived from N,N′-diphenyl-C-phenylazoformazan[5] is completely inconsistent with this hypothesis and demands the cyclic structure for **6** and **7**.



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Experimental Section

The C-carbethoxyformazans were obtained by standard procedures.[10]

N,N'-Bis(4-methoxyphenyl)-C-carbethoxyformazan had mp 131–132°. *Anal.* Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.44; H, 5.59; N, 15.91.

N,N'-Bis(4-nitrophenyl)-C-carbethoxyformazan had mp 208–210°. *Anal.* Calcd for $C_{16}H_{20}N_6O_6$: C, 49.74; H, 3.65; N, 21.75. Found: C, 49.68; H, 3.53; N, 22.45.

The ^{15}N-labeled N,N'-diphenyl-C-carbethoxyformazan and N,N'-bis(3,5-dichlorophenyl)-C-carbethoxyformazan were prepared by the same procedure using $Na^{15}NO_2$ for the diazotization of aniline or 3,5-dichloroaniline.

The ^{15}N-labeled N,N',C-triphenylformazan was prepared by the reaction of labeled benzene diazonium chloride (aniline and $Na^{15}NO_2$) with malonic acid.[11]

The tetrazolinyl radicals were generated by reaction of 0.2 ml of the formazan (0.001 *M*) in benzene with 0.2 ml of a 0.005 *M* solution of tetra-*p*-tolylhydrazine in benzene. The mixture was deoxygenated in a fused silica esr cell by a stream of prepurified nitrogen for 10 min. After closing the cell the mixture was heated to 60° for 10 sec (or the mixture was allowed to stand for 30 min at room temperature). The red-brown color of the solution changed into greenish brown after completion of the reaction.

Registry No.—N,N'-Bis(4-methoxyphenyl)-C-carbethoxyformazan, 16626-70-3; N,N'-bis(4-nitrophenyl)-C-carbethoxyformazan, 16626-71-4.

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Solvent Effects on the Oxidation of Alkyl Radicals by Lead(IV) and Copper(II) Complexes

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Received January 15, 1968

Oxidative decarboxylation of acids by lead(IV) acetate has been used to study solvent effects on the oxidation alkyl radicals by Pb^{IV} species. In the presence of copper catalyst, the rapid oxidation of alkyl radicals by Cu^{II} overwhelms the oxidation by Pb^{IV}. In both cases, alkenes (elimination) and alkyl esters (substitution) are products of electron-transfer oxidation of alkyl radicals by either Pb^{IV} or Cu^{II} oxidants. Homoallylic C_4H_7 radicals were chosen for study, since they represent optimum examples in which to observe these competing oxidative processes. Oxidative elimination of cyclobutyl radicals affords cyclobutene, whereas oxidative substitution produces a mixture of cyclobutyl, cyclopropylmethyl, and allylcarbinyl esters. Solvent effects on oxidative elimination and substitution of cyclobutyl radicals by Pb^{IV} as well as Cu^{II} have been scrutinized in order to differentiate these oxidants. Pb^{IV} is rather insensitive to solvent changes, and oxidative substitution is the preferred course of oxidation. The oxidation of cyclobutyl radicals by Cu^{II} species is highly dependent on solvent. In ethyl acetate or benzene, oxidative elimination to cyclobutene persists, whereas in acetonitrile oxidative substitution results. The dichotomy between oxidative elimination and substitution is resolved by a general mechanism which generally pertains to the oxidation of alkyl radicals by Pb^{IV} and Cu^{II}.

The decarboxylation of various acids by lead(IV) tetraacetate in benzene solutions has been induced thermally and photochemically.[1] A free-radical chain process prevails under these conditions, and the relevant propagation sequence has been postulated[1-3] as shown in eq 1 and 2. The kinetic chain length of the

$$R\cdot + Pb^{IV}O_2CR \longrightarrow R_{ox} + Pb^{III}O_2CR \qquad (1)$$

$$Pb^{III}O_2CR \longrightarrow Pb^{II} + CO_2 + R\cdot, \text{ etc.} \qquad (2)$$

$$R_{ox} = \text{alkene, ester}$$

decarboxylation is principally related to the facility of the oxidation step (eq 1). Decarboxylation of primary and secondary acids are relatively slow and exhibit short chain lengths. In contrast, tertiary and those acids which yield radicals such as benzyl and allyl, decarboxylate readily and have long chain lengths.[1,4] Generally speaking, primary and secondary alkyl radicals are not readily oxidized by Pb^{IV}, and alkanes (RH) usually result during decarboxylation of such acids by Pb^{IV}. Long chain lengths in decarboxylation are primarily correlated with high yields of oxidation products (R_{ox}).

By the same token, the decarboxylation of primary and secondary acids is markedly catalyzed by copper salts,[2,5] whereas the decarboxylation of tertiary and related acids is little affected under the same conditions.[4] Copper catalysis has been attributed to the efficient interception of alkyl radicals by Cu^{II} (eq 3) and subsequent reduction of Pb^{IV} (eq 4). In this manner,

$$R\cdot + Cu^{II} \longrightarrow R_{ox} + Cu^{I} \qquad (3)$$

$$Cu^{I} + Pb^{IV}O_2CR \longrightarrow Cu^{II} + Pb^{III}O_2CR, \text{ etc.} \qquad (4)$$

the comparatively slow oxidation of primary and secondary alkyl radicals by Pb^{IV} (eq 1) can be circumvented, and long kinetic chain lengths for decarboxylation and high yields of oxidation products ensue. From these and other observations, it has been concluded that the rates of oxidation of alkyl radicals by Pb^{IV} are roughly in the following order: $Ph_3C\cdot$ > allyl > *t*-alkyl ≫ *sec*-alkyl > primary alkyl.[1,3,4]

The kinetics and products of oxidation of alkyl radicals by Cu^{II} can also be studied by an independent method using diacyl peroxides as the source of radicals.[6] Such measurements have shown that the rates of oxidation of alkyl radicals by Cu^{II} are very fast ($k_2 > 10^8$ l. m^{-1} sec^{-1}) and are generally not highly dependent on structure.[7]

Studies of the oxidation of alkyl radicals by both Pb^{IV} and Cu^{II} using these methods indicate that two princi-

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[2] J. Kochi, *ibid.*, **87**, 3609 (1965).

[3] In the following presentation, coordination around Pb and Cu will not be given explicitly, except where pertinent to the discussion.

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