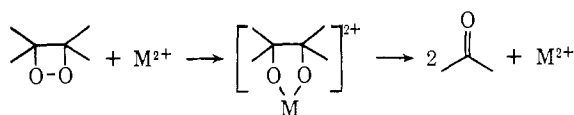
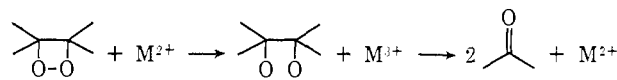


Figure 1. Linear free energy relationship for the metal ion catalyzed decomposition of TMD.

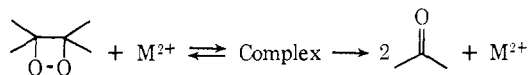
Three mechanistic possibilities can be considered for the observed catalysis: (a) insertion



(b) electron transfer



(c) coordination or Lewis acid



An insertion mechanism requires a formal two-electron oxidation of the metal ion while an electron transfer mechanism involves a one-electron oxidation. Both of these mechanisms seem unlikely because the logarithms of the second-order rate constants (k_2) do not correlate with either the third or the sum of the third and fourth ionization potentials⁹ of the neutral metals.

A coordination mechanism, involving the metal ion as a Lewis acid, is completely consistent with the counterion effect and the linear free energy relationship. Complexation of TMD by a metal ion might facilitate decomposition by removing orbital symmetry restrictions¹⁰ or by lending positive character to one or both oxygen atoms, thereby destabilizing the peroxy bond and allowing for a more facile ring cleavage.

Currently, research is in progress to determine whether the complexation involves one or both oxygen atoms of TMD. We shall report shortly on the rearrangements of TMD by strong Lewis acids.

Acknowledgments. This work was supported by grants from the National Science Foundation and the

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, p 801.

(10) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

National Institutes of Health. We thank Dr. T. Wilson for the use of her chemiluminescence-monitoring system.

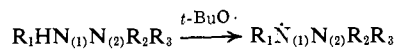
Paul D. Bartlett,* Alfons L. Baumstark, Michael E. Landis
Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138
Received May 4, 1974

Electron Paramagnetic Resonance Spectra of Alkylhydrazyl Radicals in Solution¹

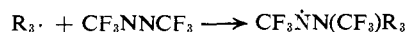
Sir:

The solution epr spectra of a great many trisubstituted hydrazyls containing aryl substituents and other electron withdrawing substituents have been known for many years.² Only recently has interest turned toward trialkylhydrazyls with Nelson and Landis' discovery³ that two bicyclic hydrazyls, $[(\text{CH}_2)_n\text{CHNN}[\text{C}(\text{CH}_3)_3]\text{CH}(\text{CH}_2)_2]$ ($n = 1$ and 2), were remarkably long lived. In this communication, we report epr spectral parameters for the first acyclic and monocyclic trialkylhydrazyls⁴ and for the first 1,2-dialkylhydrazyl to be observed in solution.

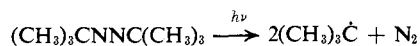
The majority of the radicals were generated by the technique we have used previously to produce 2,2-dialkylhydrazyls⁵ and 1-alkylhydrazyls,⁶ viz., photolysis of solutions of the parent hydrazines in di-*tert*-butyl peroxide directly in the cavity of an epr spectrometer.



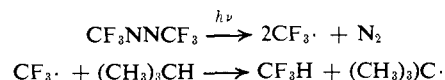
1,2-Di(trifluoromethyl)-2-alkylhydrazyls ($\text{R}_1 = \text{R}_2 = \text{CF}_3$) were prepared by alkyl radical addition to azo-trifluoromethane.



For $\text{R}_3 = t$ -butyl, the CF_3NNCF_3 was photolyzed either with azoisobutane in the absence of solvent



or in isobutane



The same spectrum was obtained in $(\text{CD}_3)_3\text{CD}$ and a closely analogous spectrum was produced in isopentane^{7,8} but not in cyclopentane (presumably be-

(1) Issued as N.R.C.C. No. 14204.

(2) For a leading review see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968. For more recent work see, e.g., A. T. Balaban and R. Istratiou, *Tetrahedron Lett.*, 1879 (1973); V. Malatesta and K. U. Ingold, *ibid.*, 3311 (1973).

(3) S. F. Nelson and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973).

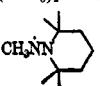
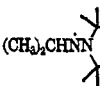

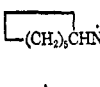
(4) Two tris(trialkylsilyl)hydrazyls, $(\text{R}_3\text{Si})\text{NN}(\text{SiR}_3)_2$, have been described very recently: R. W. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **95**, 7897 (1973).

(5) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973).

(6) V. Malatesta, D. Lindsay, E. C. Horswill, and K. U. Ingold, *Can. J. Chem.*, **52**, 864 (1974).

(7) Unless oxygen and hydroperoxides are carefully eliminated the corresponding hydrazoxyl radical is formed,⁹ $\text{CF}_3\text{N}(\dot{\text{O}})\text{N}(\text{CF}_3)\text{R}_3$; $g = 2.0062$; $a^{\text{N}} = 1.3$ and 11.9 ; $a^{\text{F}}(3\text{F}) = 2.4, 7.4$ G. This radical is stable indefinitely at room temperature. At low concentrations it disappears temporarily during photolysis.

Table I. Hyperfine Splittings (in Gauss) for Some Hydrazyl Radicals, $R_1\dot{N}_{(1)}N_{(2)}R_2R_3$, in Solution at Ambient Temperatures^a

Radical	$a^{N(1)}$	$a^{N(2)}$	a^{R_1}	a^{R_2}	a^{R_3}
$CH_3\dot{N}N(CH_3)_2$	11.7	10.5	17.6 (3 H)	5.9 (3 H)	8.2 (3 H)
$(CH_3)_2CH\dot{N}N(CH_3)_2$	11.8	10.1	11.6 (1 H)	5.5 (3 H)	7.0 (3 H)
	12.0	10.0	18.2 (3 H)		
	12.65	9.4	7.0 (1 H)		
	17.8 ^b	9.3	7.0 (1 H)		
	12.6	9.4	6.2 (1 H)		
$CF_3\dot{N}N(CF_3)C(CH_3)_3$	12.3 ^c	8.9 ^c	15.5 (3 F)	11.4 (3 F)	
$CF_3\dot{N}N(CF_3)C(CH_3)_2C_2H_5$	12.4 ^c	8.9 ^c	15.5 (3 F)	11.7 (3 F)	
$CH_3\dot{N}NH_2$ ^d	14.0	7.9	17.7 (3 H)	1.3 (1 H)	2.8 (1 H)
$H\dot{N}N(CH_3)_2$ ^e	9.6	11.5	13.7 (1 H)		6.9 (6 H)
$(CH_3)_2CH\dot{N}NH[CH(CH_3)_2]$	12.7 ^f	9.1 ^f	10.5 (1 H)	1.2 (1 H) ^g	5.0 (1 H)

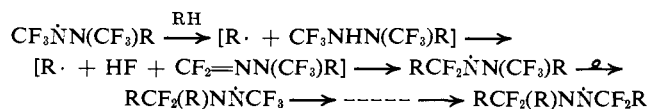
^a Satisfactory computer simulated spectra were obtained for all radicals. ^b ¹⁵N splitting (*i.e.*, a doublet splitting with almost the expected value of 1.4 for a^{15N}/a^{14N}). ^c Assignment of these nitrogens is quite arbitrary. ^d Reference 6. ^e Reference 5. ^f For assignment, see text. ^g Amino hydrogen, as shown by deuteration.

cause of slow abstraction of *sec*-H nor in toluene (presumably because the resonance stabilized benzyl radical does not add to the N=N double bond). No hydrazyl was produced by photolysis of (i) neat CF_3NNCF_3 , (ii) CF_3NNCF_3 in benzene, (iii) CF_3NNCF_3 in $(CF_3)_3COOC(CF_3)$ (a good source of CF_3 radicals), and (iv) $(CH_3)_3CN(CF_3)_3$ in $(CF_3)_3COOC(CF_3)_3$. However, photolysis of CF_3NNCF_3 , triethylborane, and di-*tert*-butyl peroxide yielded a radical that was almost certainly $CF_3\dot{N}N(CF_3)C_2H_5$. Unfortunately, a complete spectrum (432 lines if no overlap) could not be obtained in a single scan because the reactants were consumed too rapidly at light intensities sufficient to generate a reasonable epr signal.

The hyperfine splittings for some of our trialkylhydrazyls are listed in Table I together with our earlier data on $H\dot{N}N(CH_3)_2$ ⁵ and $CH_3\dot{N}NH_2$.⁶ All these radicals have *g* values of 2.0038 except for the $CF_3\dot{N}N(CF_3)R_3$ that have *g* = 2.0037.

The factors that control the conformational integrity of hydrazyls would appear to be rather nicely balanced. Thus, the majority of hydrazyls that have chemically identical groups on $N_{(2)}$ ($H\dot{N}NH_2$,⁶ $R_1\dot{N}NH_2$,⁶ $R_1\dot{N}N(R_2)_2$, and $H\dot{N}N(CH_2C_6H_5)_2$ ¹⁰) ex-

(8) On cutting off the light the hydrazyl decays ($\tau_{1/2} \sim 1$ sec) and is slowly ($\tau_{1/2} \sim 1$ min) replaced by the hydrazoxyl⁷ and a second stable (in the absence of uv light) hydrazyl: $g = 2.0034$; $a^N = 9.55, 11.45$; $a^F(2F) = 26.75, 37.5$ G. Since the same spectrum is obtained in isopentane, $(CH_3)_3CH$, and $(CD_3)_3CD$, we suggest that this radical is $RCF_2\dot{N}N(CF_2R)R$. It is probably formed by the reaction sequence

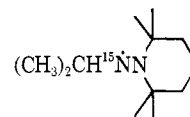


(9) For a discussion of hydrazoxyls, see V. Malatesta and K. U. Ingold, *Tetrahedron Lett.*, 3311 (1973).

(10) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 3949 (1974). In this radical the CH_2 groups may be equivalent with the magnetic inequivalence of two pairs of protons arising because the protons on each CH_2 are not equivalent.

hibit magnetic inequivalence of the two groups at ambient temperatures. Only for certain 1,1-dialkylhydrazyls ($H\dot{N}N(CH_3)_2$, $H\dot{N}N(C_2H_5)_2$, and $H\dot{N}N[CH(CH_3)_2]_2$)⁵ does this inequivalence disappear. For the $CF_3\dot{N}N(CF_3)R_3$ radicals the lines due to the CF_3 group having $a^F = 15.45$ G are broader than the other lines in the spectrum. These lines reach their expected height at $\sim 50^\circ$ and are reduced to one-third of this height at *ca.* -30° . Presumably rotation about the $N_{(1)}-CF_3$ bond is restricted. This does not appear to be the case with $CH_3\dot{N}NR_2R_3$ radicals. However, the methine coupling constants for $(CH_3)_2CH\dot{N}NR_2R_3$ radicals show that rotation of the isopropyl group is hindered particularly in the tetramethylpiperidyl derivative.

By ¹⁵N labeling, we have previously shown that in $H\dot{N}_{(1)}N_{(2)}R_2R_3$ radicals $a^{N(2)} > a^{N(1)}$,⁵ while in $R_1\dot{N}NH_2$ radicals $a^{N(1)} > a^{N(2)}$.⁶ These results were rationalized in terms of the inductive effect of the alkyl groups.^{5,6} Application of the same arguments to trialkylhydrazyls suggested that $a^{N(1)}$ should be $> a^{N(2)}$, and this was confirmed by the preparation of the



radical (see Table I).

With the nitrogens unequivocally assigned to three classes of alkylhydrazyls, it is now possible to assign nitrogen splittings to hydrazyls that have not yet been isotopically labeled or have not even been prepared (see Table II). Thus, the firm a^N data for acyclic hydrazyls gave, by linear interpolation, a^N values for 1,2-dialkylhydrazyls that were in excellent agreement with a (subsequent) measurement on 1,2-diisopropylhydrazyl. We therefore feel emboldened to extrapolate to the so-far unobserved 2-alkylhydrazyls for which we predict that $a^{N(1)} = 10.5$ and $a^{N(2)} = 10.2$ G. A

Table II. Comparison of Measured and Predicted Nitrogen Hyperfine Splittings (in Gauss) for Hydrazyl Radicals, $R_1\dot{N}_{(1)}N_{(2)}R_2R_3$, in Solution

Radical	Measured		Predicted	
	$a^{N(1)}$	$a^{N(2)}$	$a^{N(1)}$	$a^{N(2)}$
1 $H\dot{N}NH_2$	11.7 ^{a,b}	8.8 ^{a,b}	11.5 ^c	8.9 ^d
2 $H\dot{N}NHR$			10.5 ^e	10.2 ^f
3 $H\dot{N}NR_2$	9.8 ^g	11.6 ^g		
4 $R\dot{N}NR_2$	11.8 ^h	10.3 ^h		
5 $R\dot{N}NHR$	12.7 ^{b,i}	9.1 ^{b,i}	12.8 ⁱ	9.1 ^j
6 $R\dot{N}NH_2$	13.8 ^{a,k}	7.9 ^{a,k}		

^a Reference 6. ^b Assigned to conform to predicted values. ^c Calculated from $a^{N(1)}$ values for 3, 4, and 6 by the relation $1 = 3 + 3[(6 - 4)/4]$. ^d Calculated from $a^{N(2)}$ values by the relation $1 = 6 + 6[(3 - 4)/4]$. ^e Calculated from $2 = 3 + 3[(5 - 4)/4]$. ^f Calculated from $2 = 5 + 5[(3 - 4)/4]$. ^g Average values for R = Me and *i*-Pr from ref 5, plus R = Et from ref 10. ^h This work. Average of values for acyclic trialkylhydrazyls, *i.e.*, $R_1 = Me$ and *i*-Pr with $R_2 = R_3 = Me$. ⁱ This work. R = *i*-Pr. ^j Linear interpolation in the series 3, 4, 5, and 6. ^k Average for R = Me and $PhCH_2$.

similar type of extrapolation to hydrazyl itself implies that $a^{N(1)} > a^{N(2)}$ as has also been concluded from theoretical consideration.^{11,12}

Kinetic data on the decay of some of these radicals will be reported at a later date.

(11) R. Fantechi and G. A. Helcké, *J. Chem. Soc., Faraday Trans. 2*, **68**, 924 (1972).

(12) D. E. Wood, C. A. Wood, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).

(13) N.R.C.C. Visiting scientists from the Istituto Chimica Organica, Università di Bologna, Bologna, Italy. A grant from 'Laboratorio CNR dei composti del carbonio' is gratefully acknowledged.

L. Lunazzi,¹³ K. U. Ingold*

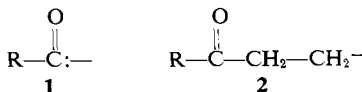
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Received March 7, 1974

Metalated Allylic Ethers as Homoenolate Anion Equivalents

Sir:

As a consequence of the central role which the carbonyl function has played in organic synthesis, chemists have endeavored to devise new synthetic methods centered around this functional group. One such area of investigation has been concerned with the design of "reversed polarity"^{1,2} equivalents. An impressive number of synthetic methods have been developed in this area which provide access to useful "carbonyl anion" (1) equivalents.^{3,4} The purpose of this com-



munication is to describe a useful approach to a related

(1) For a general discussion of reversed polarity equivalents see D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, **7**, 147 (1974).

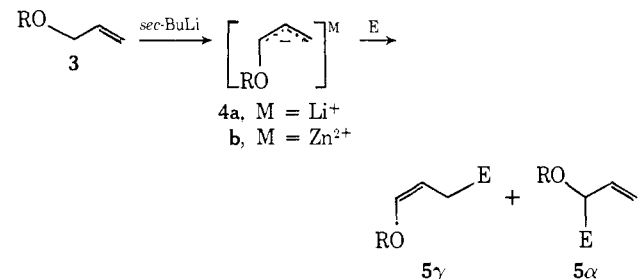
(2) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).

(3) For a direct synthetic approach to 1 see L. S. Trzupsek, T. L. Newirth, E. G. Kelly, M. E. Sbarbati, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **95**, 8118 (1973), and references cited therein.

(4) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969); G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971); J. E. McMurry and J. Melton, *ibid.*, **93**, 5309 (1971); J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972); K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 3151 (1971); K. Oshima, K. Shimoi, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 2694 (1973).

reversed polarity equivalent which may be operationally equated to a homoenolate anion (2).⁵

We have found that allylic ethers, 3, may be rapidly metalated (10 min) at -65° in tetrahydrofuran (THF)⁶ with *sec*-butyllithium⁷ in essentially quantitative yield. At these temperatures the allylic anion 4a⁸ exhibited no tendency to undergo Wittig rearrangement, a reaction characteristic of these species at higher temperatures.⁹ Our observation that these anions react regioselectively with electrophiles (E) γ to oxygen to give the adduct 5 γ establishes the operational equivalency between the oxy allylic anion 4a and homoenolate anion 2 (R = H).



In alkylation reactions of 4a (E = *n*-C₆H₁₃I), we have found the product ratio, 5 γ :5 α , to be controlled by the oxygen ligand R; typical results being: R = THP, γ : α = 54:46; R = Ph, γ : α = 63:37; R = C₂H₅, γ : α = 75:25; R = *t*-Bu, γ : α = 89:11.^{10,11} The observation that such substrate steric factors are important in controlling site-reactivity in the reactions of ambident anions 4a with electrophiles is now well predated.^{1,5a,12} It appears that the product ratio, 5 γ :5 α , for alkylation reactions is rather insensitive to other reaction conditions involving a change in solvent,⁶ or temperature.

In the reactions of the oxy allylic anion 4a with carbonyl electrophiles (E = cyclohexanone), we have observed that the product ratio 5 γ :5 α is opposite to what one would predict based upon the above alkylation study: R = *t*-Bu, γ : α = 27:73; R = Ph, γ : α = 24:76; R = C₂H₅, γ : α = 70:30; R = CH₃, γ : α = 72:28.^{10,11} This change in α : γ regioselectivity in the reactions of allylic carbanions with alkyl halides in contrast to ketones has been observed elsewhere.¹³ Furthermore,

(5) For other examples of homoenolate anion equivalents see (a) E. J. Corey and D. E. Cane, *J. Org. Chem.*, **35**, 3405 (1970); (b) E. J. Corey, B. W. Erikson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971); (c) Y. Leroux and C. Roman, *Tetrahedron Lett.*, 2585 (1973); (d) K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 7926 (1973); (e) H. Ahlbrecht and G. Rauchschalbe, *Synthesis*, 417 (1973); (f) G. Sturtz, B. Corbel, and H. Normant, *C. R. Acad. Sci., Ser. C*, 277, 395 (1973).

(6) Metalation may be also carried out in ether or in pentane with added tetramethylethylenediamine (TMEDA).

(7) No appreciable ether fission was observed with this base; *cf.* G. Köbrich and A. Baumann, *Angew. Chem., Int. Ed. Engl.*, **12**, 856 (1973). Other bases such as *n*-butyllithium are ineffective metalating agents.

(8) For H nmr data on isomeric methoxy-substituted allylic anions see H. Kloosterziel and J. A. A. VanDrunen, *Recueil*, **89**, 32 (1970).

(9) (a) H. Felkin and A. Tambuté, *Tetrahedron Lett.*, 821 (1969); (b) D. R. Dimmel and S. B. Gharpure, *J. Amer. Chem. Soc.*, **93**, 3991 (1971); (c) D. R. Dimmel and S. Huang, *J. Org. Chem.*, **38**, 2756 (1973); (d) G. Courtois and L. Miginiac, *Tetrahedron Lett.*, 2411 (1972); (e) V. Rautenstrauch, *Helv. Chim. Acta*, **55**, 594 (1972); see correction, *ibid.*, **55**, 3064 (1972).

(10) In a number of experiments the average yields of 5 α + 5 γ ranged from 75 to 95%.

(11) Satisfactory spectra and elemental analyses were obtained on all compounds reported herein.

(12) (a) E. J. Corey and D. E. Cane, *J. Org. Chem.*, **34**, 3053 (1969); (b) E. J. Corey and H. A. Kirst, *Tetrahedron Lett.*, 5041 (1968).

(13) R. Kow and M. W. Rathke, *J. Amer. Chem. Soc.*, **95**, 2715 (1973); P. E. Pfeffer, L. S. Silbert, and E. Kinsel, *Tetrahedron Lett.*, 1163 (1973).