Stable Free Radicals. VIII.[1] New Imino, Amidino, and Carbamoyl Nitroxides

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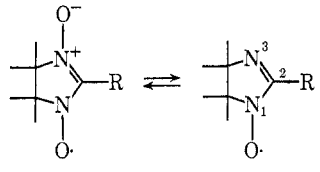
Received July 13, 1970

A new group of cyclic nitroxides **2**, **9**, and **10** are described. Many of these radicals are highly stable and undergo reactions at sites of high spin density without decomposition. Hyperfine splittings of the two ring nitrogens are changed in opposite directions by changes in the substituent. Hammett σ_p and σ_p^+ correlations are obtained. The new radicals are basic and the conjugate acids undergo proton exchange that is rapid on the esr time scale except in very acidic solutions. In bromo and iodo substituted derivatives, infrequently observed coupling to halogen was resolved.

Part A

Recently there has been described a new class of stable chemically versatile free radicals, the nitronyl nitroxides **1**.[1,3] In this paper we describe the preparation, chemistry, and spectral properties of related highly stable imino, amidino, and carbamoyl nitroxides. Although the esr spectra of some related linear radicals have been reported, the compounds were unstable and could not be chemically characterized.[4,5]

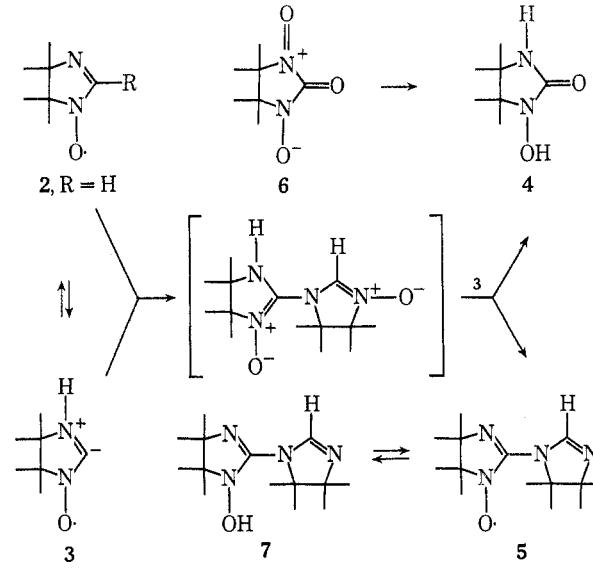
Heating nitronyl nitroxides **1** with triphenylphosphine in benzene or treatment with nitrous acid affords 4,4,5,5-tetramethylimidazoline-1-oxyls **2** in high yields. Most of these compounds are stable, low-melting orange solids which, in several cases, R = C_6H_5, CH_3, and $CH(CH_3)_2$, have been reconverted to the starting nitronyl nitroxides with *m*-chloroperbenzoic acid. The compounds are weak bases by virtue of the imino nitrogen



1 **2**

and may be reversibly protonated without decomposition or disproportionation; pK_a (**2**, R = C_6H_5) = 1.9 ± 0.1.

The unsubstituted derivative **2**, R = H, undergoes deuterium exchange at C_2 within 6 hr at pH 7. The absence of a dramatic rate increase up to pH 13 suggests a nonbase-catalyzed exchange process possibly involving the radical zwitterion intermediate **3**. Similar nonradical intermediates have recently been implicated in exchange reactions of other heterocycles.[6] Formation of **3** may also account for the spontaneous decomposition of **2**, R = H, which occurs when the pure solid is permitted to stand for 24 hr at room temperature. Two products were obtained, both in 70% yield. Identification of the hydroxyurea **4** [ν_{KBr} 1700 cm^{-1} (C=O)] was confirmed by an independent synthesis



2, R = H **6** **4**

3 **7** **5**

through reduction of the zwitterion **6**[3b] with triphenylphosphine in methanol. The radical product **5** showed esr coupling similar to the other imino nitroxides **2** (Table I). Despite the absence of coupling with the nonradical ring nitrogens, attachment of the nonradical ring in **5** through a nitrogen atom is supported by the

TABLE I

HYPERFINE SPLITTING (GAUSS) OF IMINO AND AMIDINO NITROXIDES IN BENZENE

Compd	$a_{N(1)}$	$a_{N(3)}$	a_R
2, R = $NHCH(CH_3)_2$	10.80	3.15	
2, R = $N(CH_3)_2$	10.44	3.12	
2, R = NH_2	10.40	3.38	
5	10.25	3.25	
2, R = OCH_3	9.55	3.20	
2, R = $C(CH_3)_3$	9.48	3.94	
2, R = CH_3	9.25	3.9	1.95 (CH_3)
2, R = $CH_2CH(CH_3)_2$	9.24	4.00	1.50 (CH_2)
2, R = $CH(CH_3)_2$	9.25	4.00	1.25 (CH)
2, R = C_6H_5	9.10	4.37	
2, R = H	8.80	4.40	1.5 (H)
2, R = I	8.90[a]	4.18[a]	3.9 (I)[b]
2, R = Br	8.80	4.25	1.9 (Br)
2, R = $COOCH_3$	8.50	4.33	
2, R = CN	8.00	4.63	

[a] Determined from a seven-line pattern in toluene at −70°. [b] Separation of the two lines due to iodine at 77° in benzene (see text).

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(1) Paper VII: P. W. Kopf, R. Kreilick, D. G. B. Boocock, and E. F. Ullman, *J. Amer. Chem. Soc.*, **92**, 4531 (1970).

(2) Synvar Postdoctoral Fellow, 1969–1970.

(3) (a) J. H. Osiecki and E. F. Ullman, *ibid.*, **90**, 1078 (1968); (b) D. G. B. Boocock and E. F. Ullman, *ibid.*, **90**, 6873 (1968); (c) D. G. B. Boocock, R. Darcy, and E. F. Ullman, *ibid.*, **90**, 5945 (1968); (d) E. F. Ullman and D. G. B. Boocock, *Chem. Commun.*, 1161 (1969).

(4) H. G. Aurich, *Ber.*, **101**, 1761, 1770 (1968).

(5) (a) A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965, p 123; (b) *ibid.*, p 128; (c) V. S. Griffiths and G. R. Parlett, *J. Chem. Soc. B*, 997 (1969).

(6) R. A. Cofburn, J. M. Landesberg, D. S. Kemp, and R. A. Olofson, *Tetrahedron*, **26**, 685 (1970).

TABLE II

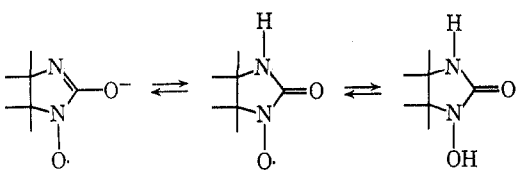
EFFECT OF pH ON HYPERFINE SPLITTING (GAUSS) OF IMINO, AMIDINO, AND CARBAMOYL NITROXIDES IN WATER

Compd	pH	$a_{N(1)}$	$a_{N(3)}$	$a_{N(exo)}$	$a_{H(3)}$	$a_{X(exo)}$
2, R = $NHCH(CH_3)_2$[a]	9	11.45	3.06	<0.5		
	b	12.97[c]	1.75[d]	<0.5		
2, R = $N(CH_3)_2$	9	11.03	3.12	<0.5		
	2	8.9	1.7	1.3[e,f]	2.0[e,f]	1.7 (CH_3)[e,f]
2, R = NH_2	9	11.00	3.31	<0.5		
	2	8.7	2.0	<0.5	3.8[f]	1.0 (H)[f]
	b	12.55[c]	2.1[d]	<0.5		
2, R = C_6H_5	7.6	9.90	4.35			
	−0.8	6.60	4.60		4.6	
9	7	10.4	1.60		1.90[f]	
	13	12.08	2.64			

[a] Spectrum in acid complex and uninterpreted. [b] Dimethyl sulfoxide–potassium *tert*-butoxide. [c] Based on solvent shifts of neutral compound a solvent correction of 0.45 G must be added to obtain coupling in water. [d] Coupling of neutral compound nearly solvent invariant. [e] Determined from spectrum of 2, R = $^{15}N(CH_3)_2$. [f] Determined from spectra taken in D_2O.

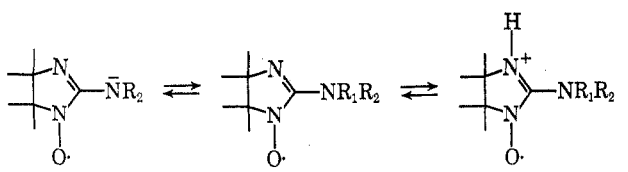
appearance of an olefinic proton in the nmr spectrum of its hydrogenation (Pd–C) product **7**.

Treatment of **2**, R = H, with sodium methoxide in methanol in the presence of air gave **2**, R = OCH_3, in 26% yield. This radical formed in higher yield (62%) from methoxide treatment of **2**, R = Br. Similarly, aqueous potassium hydroxide converted **2**, R = Br, to the radical anion **8** which on neutralization afforded the unisolated carbamoyl nitroxide **9** ($pK_a \simeq 11.0$). The identity of **9** was established by hydrogenation to give **4** from which it could be regenerated with sodium periodate.



8 **9** **4**

Stable amidino nitroxides **10** were prepared by refluxing **2**, R = Br, with aqueous amines followed by lead dioxide reoxidation of the partially reduced products. Nitrous acid reduction of amino nitronyl nitroxides **1**, R = NR_1R_2,[7] also gave the amidino nitroxides **10**. These orange radicals are moderately strong bases (**10**, $R_1 = R_2 = H$, pK_a 6.4; **10**, $R_1 = R_2 = CH_3$, pK_a 6.8) which reversibly form stable yellow radical cations **11**. It is also possible to form blue radical anions **12** from **10**, R_1 = H, by treatment with potassium *tert*-butoxide in dimethyl sulfoxide.



12 **10** **11**

The esr spectra of the new radicals (Tables I and II) display several interesting characteristics. Rarely observed coupling with heavy halogen atoms is present in the spectra of **2**, R = Br and I. Prior reports of bromine and iodine coupling are confined to some σ-iminoxyl radicals[8] and the π radical **1**, R = Br.[3b] The spectrum of **2**, R = Br, is fully resolved in most solvents at room temperature except in water and dimethyl sulfoxide where only two of the four bromine lines (I = 3/2) are observed. The spectrum of **2**, R = I, is highly sensitive to solvent and temperature. Only two of the six lines expected due to iodine coupling (I = 5/2) are observed even under the best conditions for spectral resolution (Table I). The ability to resolve halogen hyperfine interactions in these and other halo radicals may be related to d orbital bonding which may reduce the electric field gradients at the halogen nuclei.

Hyperfine coupling of the ring nitrogens in **2** and **10** correlate with the electronic properties of the 2 substituents. Coupling with the nitroxide nitrogen decreases with substituent electron-withdrawing capacity (σ_p) due to coulombic destabilization of the $\dot{N}$–$\bar{O}$ resonance form. On the other hand, electron-donating capacity of the substituents decreases coupling to the imino nitrogen through reduction of the C=N bond order. The approximate fraction of nitrogen spin density located on N_3 [*vis.*, $a_{N(3)}/(a_{N(1)} + a_{N(3)})$] correlates best with σ_p^+.

The esr spectra of the amidino nitroxides **5** and **10** are unusual in that only two nitrogens show coupling. The dependence of N_3 coupling on C=N bond order and the absence of coupling with substituents on the exocyclic nitrogen suggest that coupling occurs only with the ring nitrogens. Surprisingly, even when there is multiple bond character toward both N_3 and the exo nitrogen as in the ions **11**, $R_1 = R_2 = H$, and **12**, R_2 = H and $CH(CH_3)_2$, there is coupling to only two nitrogens. Although coupling to all nitrogens occurs in the cations **11**, $R_1 = R_2 = CH_3$ and R_1 = H, $R_2 = CH(CH_3)_2$ (Table II) at least in the former, coupling is weaker to the exo nitrogen than to N_3. The reason for weak exo nitrogen coupling in **11** and **12** is uncertain. Possibly angular distortions at C_2 and N_3 imposed by the five-membered ring have a strong influence on the distribution of spin density although transannular spin transmission through space or through σ bonds cannot be ruled out.

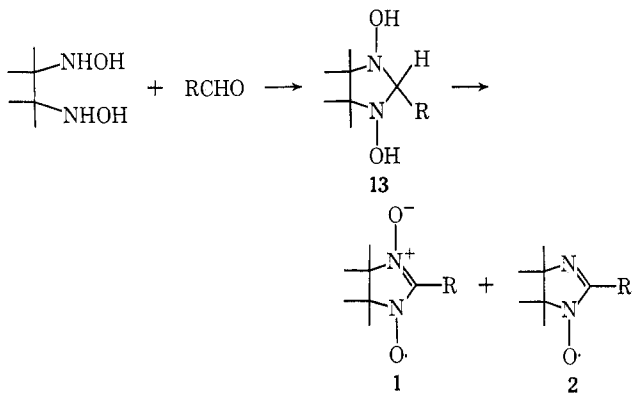
Part B

Preparation and Chemical Properties.—Members of the new class of imino nitroxides **2** were first observed

(7) Unpublished observations of L. Call.

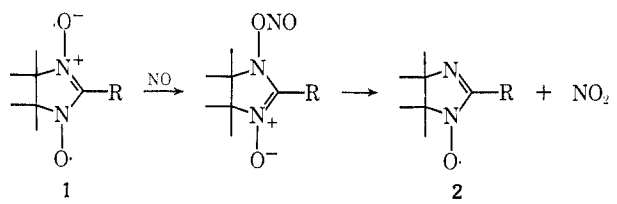
(8) (a) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965); (b) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); (c) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 981 (1967); (d) *ibid.*, 123 (1968).

as by-products during the synthesis of nitronyl nitroxides[3] **1** from lead dioxide or sodium periodate oxidation of *N,N'*-dihydroxyimidazolidines **13**. These compounds are the first examples of stable imino nitroxide radicals. Chemical evidence for their structures is provided by ready interconversions with the



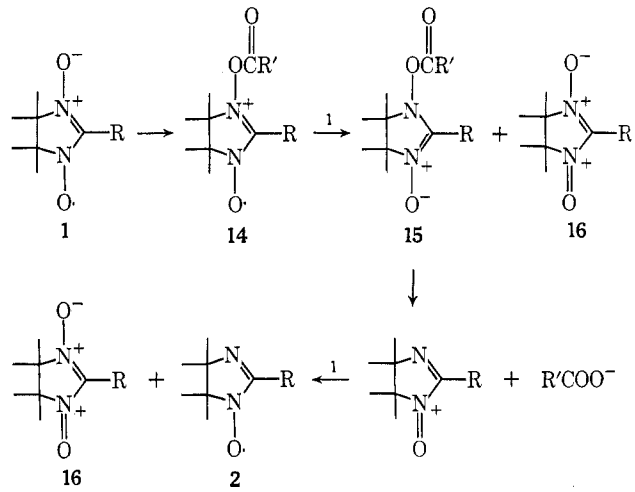
corresponding nitronyl nitroxides **1** which occur under a variety of conditions. Thus, in addition to the above described deoxygenation of **1** with triphenylphosphine or nitrous acid, the imino nitroxides **2** are also formed from **1** with active acid derivatives such as acid chlorides or anhydrides or sulfonylisocyanates, with lead dioxide and acetic acid in dimethylformamide, and occasionally simply by heating. The absence of rearrangement during these reactions is confirmed by reoxidation of the imino nitroxides **2** to nitronyl nitroxides **1** with *m*-chloroperbenzoic acid or with hydrogen peroxide and a catalytic amount of phosphotungstic acid.

Except for the use of triphenylphosphine, none of the above conditions had been predicted to lead to the formation of imino nitroxides, and only limited evidence is available concerning the course of the reactions. Although the formation of imino nitroxides during oxidation of the imidazolidines **13** obviously requires a dehydration step, the mechanistic details are uncertain. On the other hand, partial evidence for the active species in the deoxygenation of nitronyl nitroxides **1** with nitrous acid is available from the observation that nitric oxide alone effects this reaction.



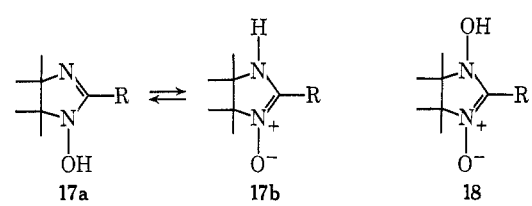
The ability of active acid derivatives to deoxygenate nitronyl nitroxides **1** is consistent with the weak basic properties of these compounds.[3a] Thus an acyl derivative **14** may initially be formed which could then accept an electron from unreacted **1** with formation of the known cation **16**.[3a] Heterolytic cleavage of the acyl product **15** followed by a second electron transfer could account for the imino nitroxide product.

Partial evidence in support of the latter mechanism was obtained from room temperature reaction of **1**, R = C_6H_5, with *p*-toluenesulfonyl isocyanate in methylene chloride to give a 48% conversion to **2**, R = C_6H_5. When this reaction was stopped prior to completion a



yellow, highly polar intermediate was observed. Since this intermediate underwent reaction with ethers and alcohols to give **1**, R = C_6H_5, it was very probably the cation **16**, R = C_6H_5.[3a] The latter compound is a very strong oxidizing agent and even reacts slowly with water to give back the nitronyl nitroxide **1**, R = C_6H_5. The formation of the imino nitroxide **2**, R = C_6H_5, in greater than 33% yield may be due to slow reduction of **16**, R = C_6H_5, by solvent impurity or by the as yet undefined product derived from the sulfonyl isocyanate reagent.

The imino nitroxides **2** have equal or greater thermal stability than the nitronyl nitroxides **1**, and many of them survive heating above 100° in neutral or alkaline solutions without appreciable decomposition. Like the nitronyl nitroxides **1**, imino nitroxides **2** can be quantitatively reduced by catalytic hydrogenation with the uptake of one atom equivalent of hydrogen. The resulting reduced modifications can in principle exist in two tautomeric forms. The phenyl derivative **17**, R = C_6H_5, has been studied in this regard. It appears to exist principally in the amidino oxide form **17b**, R = C_6H_5, since in dilute solutions its ultraviolet absorption is nearly identical with that of the reduced nitronyl nitroxide **18**, R = C_6H_5. However, as its solutions do not obey Beer's Law, the distinction between the two forms



in concentrated solution may be obscured by intermolecular hydrogen bonding. The reduced imino nitroxides **17** are less readily reoxidized than their nitronyl nitroxide counterparts **18**[3a] as demonstrated by their relative stability in air and the inability of **17b**, R = C_6H_5, to reduce the phenyl nitronyl nitroxide **1**, R = C_6H_5.

Esr Spectra.—The imino nitroxides **2** and **10** display coupling to both nitrogens. These couplings give rise to nine major lines which frequently overlap to give a seven-line pattern (Figures 1–3). Coupling with the *gem*-methyl hydrogens is weak (~0.2 G) and usually unresolved. Alkyl substituents at the 2 position display α-hydrogen coupling which decreases in the order

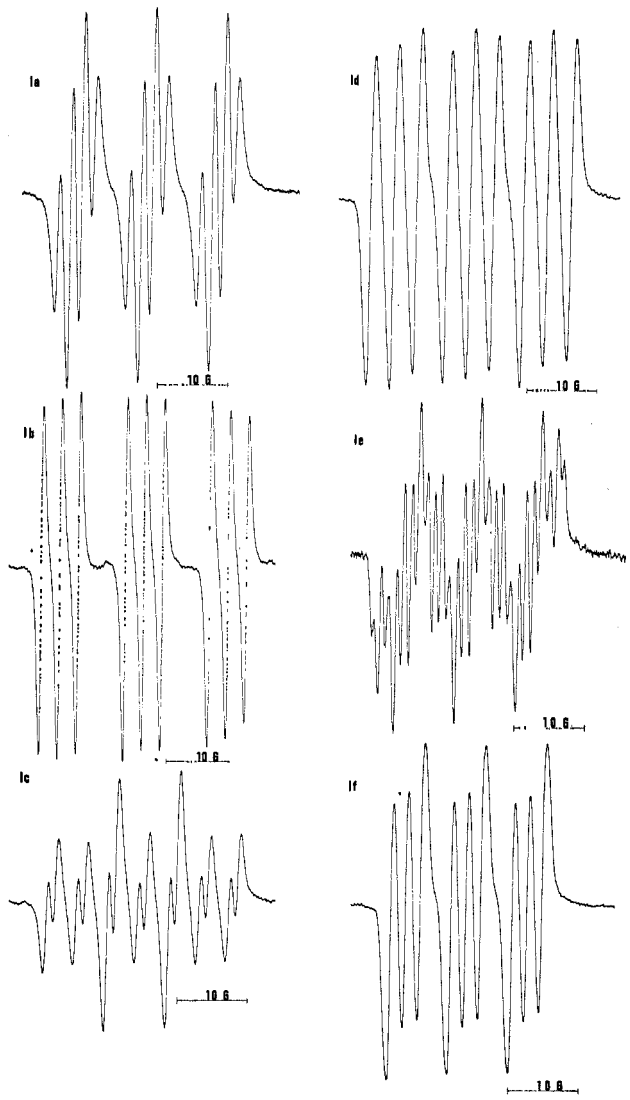


Figure 1.—Esr spectra of (a) carbamoyl nitroxide **9** in water; (b) **9** in 0.1 *N* NaOH; (c) imino nitroxide **2**, R = H in benzene; (d) **2**, R = NH_2 in pH 9 buffer; (e) **2**, R = NH_2 in pH 2 buffer; (f) **2**, R = NH_2 in pD 2 buffered D_2O.

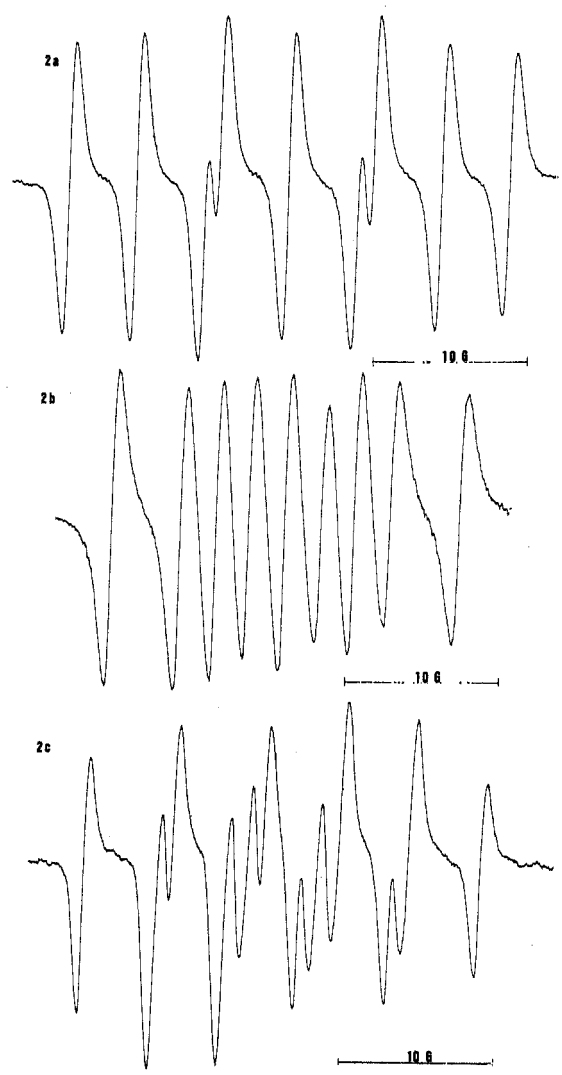


Figure 2.—Esr spectra of imino nitroxide **2**, R = C_6H_5, in (a) pH 7.6 buffer; (b) pH 1.4 buffer; (c) 6 *N* HCl.

methyl > methylene > methine (Table I) due undoubtedly to increased steric hinderance to overlap of the C–H bonds with the C_2 π orbital.

Previously reported spectra of linear imino nitroxides[4] also display coupling with both nitrogens. In these less stable derivatives, the nitrogen coupling constants are strongly affected by steric factors which interfere with coplanarity of the system. Previously reported linear amidino[5a] and carbamoyl[5c] nitroxides display coupling with only one nitrogen presumably for similar reasons. In the present cyclic compounds, coplanarity is assured and the effects of substituents and solvents can be attributed primarily to their electronic properties. Examination of these effects reveals that **2** and **10**, like simple nitroxides,[9] show an increase in the nitroxide nitrogen coupling constants $a_{N(1)}$ with increasing solvent polarity (Table III). This is consistent with the expected increase in stabilization of $\overset{\cdot}{N}-\overset{+}{O}$ resonance contributors in more polar media. With the exception of the amino derivatives **10**, increased solvent polarity produces a similar effect on $a_{N(3)}$ due to partial resonance delocalization of the increased N_1 spin density (*cf.* Tables I–III). The effect of introduction of electron-donating substituents at the 2 position also is to increase $a_{N(1)}$, but now there is a decrease in N_3 coupling (Table I).

Interpretation of these results is simplified by assuming that the spin density in **2** is distributed only on

(9) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 198.

TABLE III

EFFECT OF SOLVENTS ON NITROGEN HYPERFINE COUPLING (GAUSS) IN **2**, R = $C(CH_3)_3$

Solvent	E_T[a]	$a_{N(1)}$	$a_{N(3)}$
Water[b]	63.1	10.20	4.23
Formamide	56.6	9.84	4.12
Ethanol[b]	51.9	9.47	4.08
Acetonitrile	46.3	9.70	3.93
Methylene chloride	41.1	9.65	3.98
Chloroform	39.1	9.65	3.98
Ethyl ether	34.6	9.40	3.80
Benzene	34.5	9.48	3.94
Carbon tetrachloride	32.5	9.32	3.90
n-Hexane	30.9	9.30	3.87

[a] Solvent polarity parameter: see C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965). [b] Protonic solvents may have unrepresentative coupling due to hydrogen bonding to N_3 which shifts free spin density away from N_1.

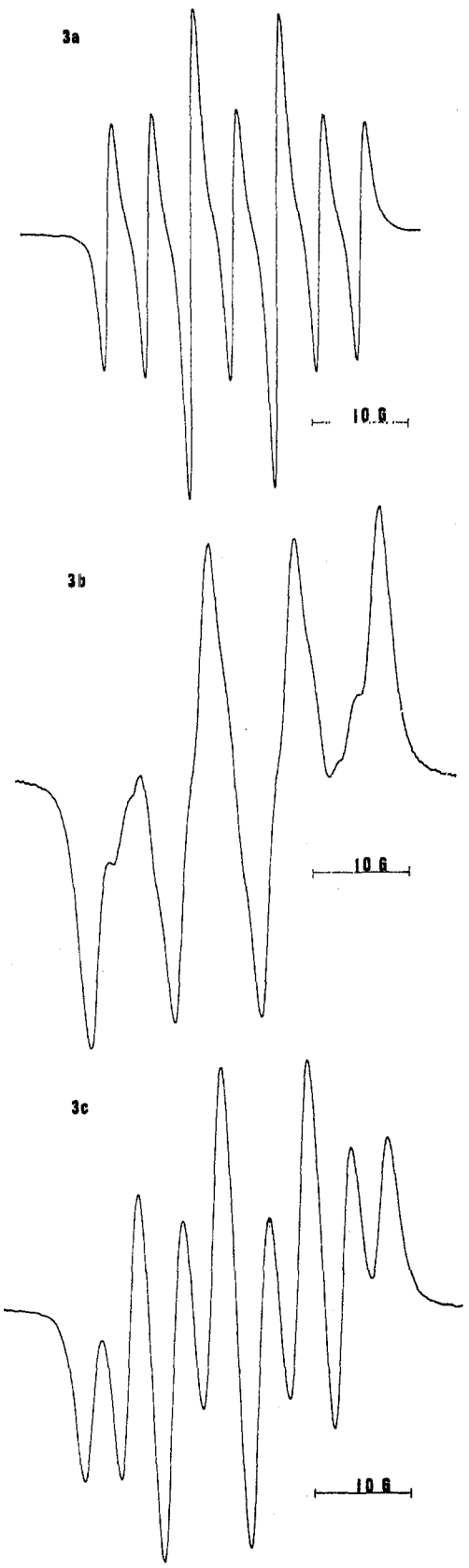


Figure 3.—Esr spectra of imino nitroxide **2**, R = I in toluene at (a) −70°; (b) 18°; (c) 77°.

O, N_1, and N_3. Based on the simplified Karplus–Fraenkel expression (eq 1),[10,11] coupling to N_1 is given

$$a_N = Q^N_N \rho_N + \sum_i Q^N_{X(i)} \rho_{X(i)} \quad (1)$$

$$a_{N(1)} = Q^N_{N(1)} \rho_{N(1)} + Q^N_{ON} (1 - \rho_{N(1)} - \rho_{N(3)}) \quad (2)$$

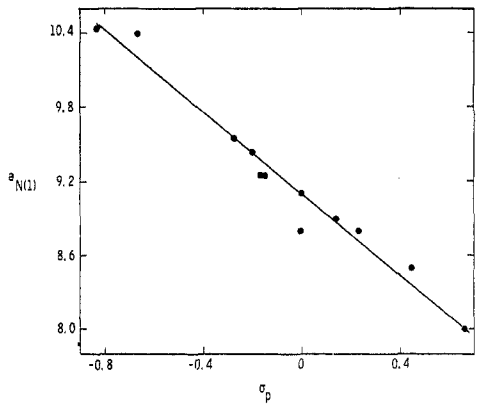


Figure 4.—Effect of substituents on hyperfine coupling of N_1 in the imino nitroxides **2**. σ_p values taken from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

by eq 2. Since $Q^N_{N(1)}$ is 10–20 times[12] greater than Q^N_{ON}, and $\rho_{N(1)}$ is expected to be greater than $\rho_{N(3)}$, coupling to N_1 should be approximately proportional to its spin density $\rho_{N(1)}$. The observed correlation of $a_{N(1)}$ with σ_p values of the 2 substituents (Figure 4) is consistent with this relationship and suggests that spin density at N_1 is controlled by substituent inductive effects.[13]

Distribution of spin density to N_3 might, on the other hand, be expected to depend primarily on the C=N bond order. This should be reduced by resonance interactions with the 2 substituents. The effect is exemplified by the substituent effects given in Table I, the reduction in the $a_{N(3)}$ coupling of **10** on either protonation or deprotonation, and the increase in $a_{N(3)}$ of the carbamoyl nitroxide **9** upon deprotonation (Table II). The small $a_{N(3)}$ solvent dependence of the amino derivatives **10** (*cf.* Tables I and II) also fits this picture. Higher N_3 spin density in more polar solvents would be expected by partial distribution of the increased N_1 spin. This is offset by transmission of a smaller fraction of the spin to N_3 because the same solvents increase resonance delocalization of the amino group and reduce the C=N bond order.

The spin density $\rho_{N(3)}$ is expected to be approximately proportional to $a_{N(3)}$ (eq 3).[11,12] Since spin

$$a_{N(3)} = Q^N_{N(3)} \rho_{N(3)} \quad (3)$$

$$a_{N(1)} = Q^N_{N(1)} \rho_{N(1)} \quad (4)$$

distribution to N_3 will be reduced by the donation of electrons into the C=N bond, we might expect a correlation of $a_{N(3)}$ with σ_p^+. Although $a_{N(3)}$ does indeed correlate better with ρ_p^+ than with other Hammett parameters, the correlation is only fair (correlation coefficient 0.847). It is found that the ratio $a_{N(3)}/[a_{N(1)} + a_{N(3)}]$ correlates significantly better (Figure 5). The result is rationalized by use of eq 4 where the small Q^N_{ON} terms in (eq 2) have been neglected. If we assume that $Q^N_{N(1)} \cong Q^N_{N(3)}$, then $a_{N(3)}/[a_{N(1)} + a_{N(3)}]$ becomes a measure of the spin distribution between N_1

(10) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).
(11) P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963).
(12) (a) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962); (b) P. B. Ayscough and F. P. Sargent, *J. Chem. Soc. B*, 907, (1966).
(13) For a discussion of correlations of nitrogen coupling constants with Hammett parameters, see E. G. Janzen, *Accounts Chem. Res.*, 279 (1969).

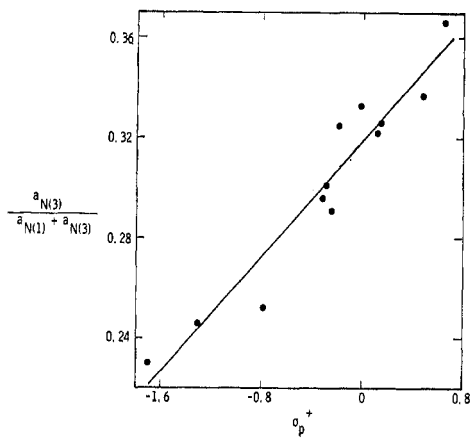


Figure 5.—Effect of substituents on the hyperfine coupling ratio $a_{N(3)}/[a_{N(1)} + a_{N(3)}]$ in the imino nitroxides **2**. σ_p^+ values taken from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

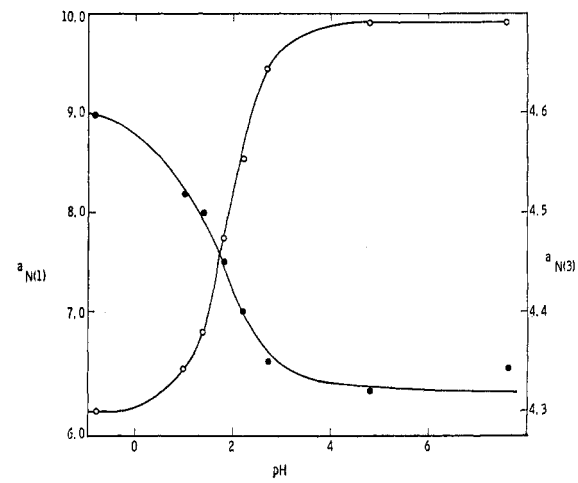


Figure 6.—Effect of pH on hyperfine coupling of **2**, R = C_6H_5: $a_{N(1)}$, open circles; $a_{N(3)}$, closed circles.

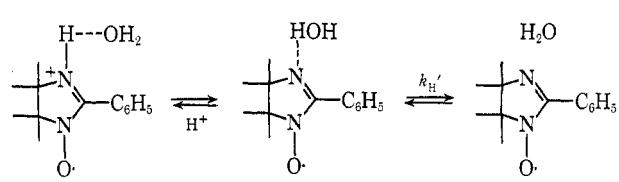
and N_3 and should be sensitive to the C=N bond order.[14]

Halogen Coupling.—The esr coupling to halogen in the imino nitroxides **2**, R = Br and I, will be described in detail elsewhere.[16] Failure to observe halogen hyperfine coupling in most bromo and iodo radicals arises from the large halogen nuclear quadrupole moments. Fluctuations in the electric field gradients at the halogen nuclei due to molecular tumbling generally produce nuclear spin relaxation rates that are greater than the hyperfine splitting, and spectral averaging of the nuclear spin states occurs. Structural features that reduce electric field gradients at the halogen nuclei should favor the observation of halogen coupling. In the present examples the nuclear field gradients caused by the asymmetric halogen σ bonds are possibly partially offset by back bonding of the symmetrical halogen d orbitals with the π system or bonding through space with the nitroxide oxygen. A similar explanation could account for the halogen coupling in the iminoxyl radicals.[8]

pH Dependence.—The imino nitroxides **2** are weak bases which can be protonated without loss of free-radical character. The esr spectrum of **2**, R = C_6H_5, was studied as a function of pH. Resolved spectra showing coupling to both nitrogens but not to the added proton were obtained above pH 1.0. At lower pH line broadening was observed and in 6 *N* hydrochloric acid coupling to the added proton became resolved (Figure 2). The coupling constants $a_{N(1)}$ and $a_{N(3)}$ changed gradually with pH giving typical titration plots from which was obtained the pK_a 1.9 ± 0.1. On lowering the pH the N_1 coupling decreased and the N_3 coupling increased (Figure 6).

The change in a_N with pH suggests that protonation occurs on the imino nitrogen. The inductive effect should reduce coupling to N_1 and increased N_3 coupling should occur by additional resonance delocalization of spin to N_3. By contrast, protonation of simple nitroxides occurs on oxygen and is known to produce increased nitroxide nitrogen coupling.[17] The observed gradual changes in nitrogen coupling without the appearance of two spectroscopically identifiable species require that the protonated and unprotonated radicals are in rapid equilibrium. Spectroscopic averaging is expected when $1/\tau \gg \sqrt{2}\,\pi\delta\nu$ where τ is the mean lifetime of the two species and $\delta\nu$ is the line separation in hertz.[18] Since $a_{N(1)}$ undergoes an overall change of 3.9 G on protonation, both protonation and deprotonation can be estimated to proceed with first-order rate constants of $\gg 5 \times 10^7$ sec^{-1}. The base causing deprotonation is not imino nitroxide since spectral averaging occurs even at very low concentrations (10^{-6} *M*). Hydroxide ion also cannot act as the base as its low concentrations also cannot account for the fast exchange rates. Accordingly, the acid counterion or water probably acts as the base.

The absence of proton coupling in protonated **2**, R = C_6H_5, at pH > 1 is also consistent with a rapid exchange process. However, the appearance of proton coupling at pH < 0 requires a mechanism which permits acid inhibition of the proton exchange despite high counterion and water concentrations. Similar inhibition of proton exchange in very acidic solutions of ammonia and amines has previously been observed.[19] The behavior has been attributed to a reduction in the equilibrium concentration of hydrogen bonded free base which is the species postulated to undergo exchange. A similar explanation where acid lowers the concentration of the hydrogen bonded species **20** may account for the present observation. This mechanism is supported by the similar magnitudes of k_H' for the amines[19] and that



20

(14) This assumption is consistent with estimates of Q_N^N of 23–28 G for imino nitrogens[15] and 23–36 G for nitroxide nitrogens.[5b,12]

(15) J. R. Bolton in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968.

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(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

(19) M. T. Emerson, E. Grunwald, M. L. Kaplan, and R. A. Kromhout, *J. Amer. Chem. Soc.*, **82**, 6307 (1960).

TABLE IV

PHYSICAL PROPERTIES OF IMINO NITROXIDES 2

Substituent	Mp, °C[a]	ν (cm^{-1})[b]	λ_{max}, mμ (ϵ)[c] (l. mol^{-1} cm^{-1})
$NHCH(CH_3)$[d,e]	46–48	($CHCl_3$) 1641, 1367	(EtOH) 232 (6080), 464 (1230)
$N(CH_3)_2$[d,e]	*f*	($CHCl_3$) 1610, 1370	(EtOH) 246 (3700), 465 (510)
NH_2[d,e]	141–144	(KBr) 1685, 1367	(EtOH) 238 (4080), 440 (1100)
OCH_3[d,e]	58–59	($CHCl_3$) 1630, 1370	(C_6H_{14}) 243 (6500), 372 (1220)
$CH(CH_3)_2$	*f*	($CHCl_3$) 1590, 1370	
$CH_2CH(CH_3)_2$[e]	*f*	(CCl_4) 1588, 1365	
$C(CH_3)_3$[d,e]	44–46	(CCl_4) 1576, 1365	(C_6H_{12}) 263 (7850), 371 (660), 530 (26)
C_6H_5[d,e]	27–28	($CHCl_3$) 1600, 1370	(C_6H_{14}) 230 (16,200), 273 (3500), 304 (4300), 442 (440), 502 (190)
H[d]	53–54		
I[d,e]	95–97	($CHCl_3$) 1500, 1368	(C_6H_{12}) 267 (3800), 399 (345), 522 (19)
Br[d,e]	54	(KBr) 1520, 1370	(C_6H_{12}) 274 (6150), 387 (550), 521 (23)
CN[e]	110–113	($CHCl_3$) 1545, 1370, 2245 (C≡N)	(C_6H_{12})[g] 300, 346, 436, 496
	70–71	($CHCl_3$) 1600, 1370	

[a] Sublimation accompanies melting in most compounds. [b] Peaks for C=N and N–O stretching, respectively, are given. [c] Shoulders and vibrational structure not recorded. [d] Satisfactory elemental analysis for C, H, and N (>0.3% error). [e] Empirical formula confirmed by mass spectroscopy. [f] Oil, freezes below room temperature. [g] Accurate extinction coefficients not obtained due to slow intensity changes on dilution. Association product probably diamagnetic since the esr spectra were not distorted.

estimated for **20** (5×10^9 sec^{-1}) by determining the pH (−0.7) that produces line coalescence.

The base strengths of the amidino nitroxides **10** were determined from optical spectroscopy (see Part A). At pH's where these compounds were only partially protonated, averaging of the nitrogen coupling in the esr was again observed. At lower pH's coupling to the added proton was also resolved. Analysis of the spectra of acidic solutions of **10**, $R_1 = R_2 = H$ and $R_1 = R_2 = CH_3$, was achieved by use of deuterium oxide solvent, and in the latter case by the incorporation of ^{15}N at the 2 position (Table II). It has not been possible to interpret the spectra of acidic solutions of **10**, $R_1 = CH(CH_3)_2$, $R_2 = H$.

Optical and Mass Spectra.—The infrared spectra of **2** and **10** display strong characteristic absorption at 1365–1378 cm^{-1} attributable to the nitroxyl stretching frequency.[20] The C=N stretching peaks appear at 1576–1600 cm^{-1} in the alkyl and phenyl derivatives but move higher with the amino and methoxy substituents and lower with electron-withdrawing substituents. The ultraviolet and visible spectra of these compounds are quite variable. The strongest absorption maximum is generally found in the range 230–300 mμ with a second weaker maximum in the 370–470 mμ range. Resolution of additional maxima seems to depend strongly on substitution, and many of the spectra display long wavelength tails extending to near 600 mμ. The halo, *tert*-butyl, and phenyl derivatives give well resolved spectra with long wavelength maxima at 500–530 mμ ($\epsilon \sim 20$) and longer wavelength shoulders which may be due to n,π^* transitions (see Table IV).

Mass spectral fragmentation patterns of **2** and **10** display molecular ion peaks plus characteristic major fragments at *m/e* 114 and 84. These may be accounted for by loss of RCN followed by loss of NO.

(20) A. K. Hoffman and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961), report the N–O frequency at 1345 cm^{-1} for di-*tert*-butyl nitroxide.

Experimental Section

Representative procedures are given below for the preparation of imino nitroxides, **2**. The triphenylphosphine and nitrous acid reductions of nitronyl nitroxides **1** have general applicability, and the physical properties of the imino nitroxide products of these reactions are given in Table IV. Catalytic hydrogenation of the imino nitroxides to their reduced modifications **17** and reoxidation with lead dioxide or sodium periodate also have general utility.

The esr spectra were recorded using a Varian E3 spectrometer which operates at 9.5 G Hz. Several imino nitroxide spectra were distorted with abnormally intense outermost lines. The behavior was dependent on concentration, temperature, and solvent and could be avoided by sufficient dilution. Association of these radicals in solution was also detected by deviations from Beer's Law at high concentrations.

2-Phenyl-4,4,5,5-tetramethylimidazoline 3-Oxide (17b, R = C_6H_5).—To a solution of 1.0 g of 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide[3a] (**1**, R = C_6H_5) in 100 ml of absolute ethanol was added 7.5 ml of concentrated HCl over 15 min at room temperature. The solution was warmed on a steam bath until it became colorless (~1 hr). It was evaporated *in vacuo;* the residue was taken up in methanol and neutralized with sodium carbonate. Evaporation of the solvent and extraction of the residue with chloroform yielded 0.43 g (46%) of the product: mp 189–190° dec; nmr (DMSO) τ 2.26 (5 Ar H, m), 5.97 (NH, s), and 8.85 (4 CH_3, s); λ_{max}^{EtOH} 238 mμ (ϵ ~15,000) and 325 (~5000) (concentration dependent).

Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.51; H, 8.31; N, 12.83. Found: C, 71.37; H, 8.25; N, 12.70.

2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl (2, R = C_6H_5). **A.**—2-Phenyl-4,4,5,5-tetramethylimidazoline 3-oxide (**17b**, R = C_6H_5), 0.200 g, in 100 ml of benzene was treated with 4 g of lead dioxide with vigorous stirring at room temperature for 35 min. After filtration, the solution was evaporated *in vacuo* and the orange-brown oil chromatographed on silica gel with benzene. The orange band was collected, and evaporation of the solvent yielded the pure crystalline product (75%).

B.—2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (**1**, R = C_6H_5), 47 mg, was dissolved in 5 ml of dry dimethylformamide, and 0.25 g of sodium nitrite and 3 drops of concentrated hydrochloric acid were added. On heating the mixture on a steam bath for 10 min, the original blue color changed to orange brown. After cooling, the solution was diluted with 35 ml of benzene and stirred with 2 g of lead dioxide for 5 min at room temperature in order to reoxidize the partially reduced product. After filtration and concentration *in vacuo*, the residue was

chromatogaphed on silica gel with 1:1 benzene–ether to yield 40 mg (91%) of the radical.

This product could be reconverted to the starting nitronyl nitroxide **1**, R = C_6H_5, by stirring in a methylene chloride solution containing *m*-chloroperbenzoic acid for a few minutes at room temperature. Alternatively the imino nitroxide **2**, R = C_6H_5, was stirred for 3 days in 3% hydrogen peroxide containing a catalytic amount of phosphotungstic acid (5% of the weight of **2**, R = C_6H_5). However, the conversion is slow and incomplete under the latter conditions.

C.—To a solution of 112 mg of 2-phenyl-4,4,5,5-tetramethylimidazolidine-1-oxyl 3-oxide (**1**, R = C_6H_5) in 10 ml of dry methylene chloride was added 95 mg of *p*-toluenesulfonyl isocyanate. The reaction mixture was stirred for 16 hr under nitrogen at room temperature. The brown residue obtained by evaporation of the solvent *in vacuo* was chromatographed on silica gel with ether. The imino nitroxide **2**, R = C_6H_5, was obtained in 48% yield (50 mg).

Interruption of the reaction before completion and thin layer chromatography of the reaction solution on silica gel gave a yellow spot which did not migrate with methylene chloride, acetonitrile, or hydrocarbon solvents. However, it became blue with alcohols and ethers. This blue product was indistinguishable from the starting nitronyl nitroxide **1**, R = C_6H_5.

2-*tert*-Butyl-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl [2, R = $C(CH_3)_3$].—2,3-(Bishydroxylamino)-2,3-dimethylbutane (1.48 g) and 2.20 ml of pivalaldehyde in 10 ml of methanol were allowed to stand at room temperature for 1 day. Evaporation of the mixture *in vacuo* yielded a partly crystalline residue which was suspended in 500 ml of water containing 2.0 g of $NaHCO_3$. A solution of 3.20 g of $NaIO_4$ in 50 ml of water was added to this solution with cooling in an ice bath. After the addition was complete, the mixture was stirred for 30 min in the dark at room temperature and then extracted with four 100-ml portions of methylene chloride. The combined organic phases were dried over Na_2SO_4 and evaporated and the crystalline residue chromatographed on silica with ether. In addition to the isolation of 1.0 g of 2-*tert*-butyl-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide [**1**, R = $C(CH_3)_3$], there was obtained 400 mg (19%) of a brown-red oil. Sublimation *in vacuo* at 30° gave 370 mg of **2**, R = $C(CH_3)_3$.

4,4,5,5-Tetramethylimidazoline-1-oxyl (2, R = H). A.—To a benzene solution (125 ml) of 1.57 g of 4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (**2**, R = H) was added 3 g of triphenylphosphine. The reaction mixture was boiled for 15 min by which time the deep purple color was replaced by orange. The solvent was removed *in vacuo* and the residue chromatographed over silica gel, first by elution with CH_2Cl_2 and then with ether. The solvent was removed *in vacuo* from the pure orange product, 0.675 g (48%) which could be stored in ether solution at Dry Ice temperature. The product was completely decomposed upon standing overnight at room temperature.

B.—To 1 ml of a benzene solution containing several milligrams of 4,4,5,5-tetramethylimidazolidine-1-oxyl 3-oxide (**1**, R = H) was added two drops of pyridine and one drop of methanesulfonyl chloride. This mixture was maintained at 70° for 5 min and then allowed to stand for 1 hr at room temperature. The resulting solution was washed several times with water. The above product was separated by tlc.

1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-one (4). A.—A sample of 0.35 g of 4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = H) which was allowed to stand overnight at room temperature was extracted with ether to leave a white ether-insoluble crystalline compound. Recrystallization from methanol–ether gave the product in 70% yield (92 mg): mp 225–230°; ν_{KBr} 1700 (C=O), 3210 cm^{-1} (NH, OH); nmr (DMSO) τ 8.93 and 8.98 (4 CH_3, d), 3.36 (1 H exchanged with D_2O, s), 1.47 (1 H exchanged with D_2O, s).

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71; mol wt, 158. Found: C, 53.01; H, 8.81; H, 17.50; *m/e* 158 (M^+).

B.—A solution of 4,4,5,5-tetramethylimidazolidin-2-one-1-oxyl anion (**8**) was prepared by heating 55 mg of 2-bromo-4,4,5,5-tetramethylimidazolidine-1-oxyl (**2**, R = Br) in 10 ml of 2 *N* KOH at 70° for 20 min. Potassium borohydride (10 mg) was added and the solution stirred for 3 min at room temperature. The reaction mixture was then neutralized with 2 *N* HCl and taken to dryness *in vacuo*. Continuous extraction of the residue with ethyl acetate and evaporation of the extracts yielded 25 mg of the product.

Alternatively, a solution of the anion **8** was brought to pH 7 with HCl and extracted with ethyl acetate. This solution of radical **9** was dried over $MgSO_4$ and hydrogenated at atmospheric pressure over palladium on charcoal to give the hydroxyurea product.

C.—4,4,5,5-Tetramethylimidazolidin-2-one 1,3-dioxide (**6**)[3b] (86 mg) was dissolved in 5 ml of methanol and 131 mg of triphenylphosphine was added at 0°. The orange color of **6** faded very rapidly. The unreacted triphenylphosphine was removed by filtration and the solution concentrated *in vacuo*. The residue was purified by preparative tlc on silica gel with ether to give 25 mg (32%) of 1-hydroxy-4,4,5,5-tetramethylimidazolidin-2-one (**4**).

2-(4,4,5,5-Tetramethylimidazolidine-1-yl)-4,4,5,5-tetramethylimidazolidine-1-oxyl (5).—A sample of 0.35 g of 4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = H) which was allowed to stand overnight at room temperature was extracted with ether. The residue was nearly pure 1-hydroxy-4,4,5,5-tetramethylimidazolidine-2-one. The extracts were concentrated *in vacuo* and purified by chromatography on silica gel with ether. The solid orange product was obtained in 70% yield (0.152 g) by evaporation of the solvent and recrystallization from chloroform.

Anal. Calcd for $C_{14}H_{25}N_4O$: C, 63.36; H, 9.50; N, 21.11; mol wt, 265. Found: C, 62.85; H, 9.52; N, 20.65; *m/e* 265 $(M)^+$, 266 $(M + 1)^+$.

Reduction of 30 mg of this compound in 5 ml of ethyl acetate with hydrogen and palladium on charcoal yielded a white diamagnetic solid **7**. The nmr spectrum (CCl_4) showed signals at τ 8.9, 8.84, and 8.62 (8 CH_3) which obscured a one-proton signal (NOH) that disappeared on addition of D_2O. An additional singlet at τ 2.38 (N=CH) was unaffected by D_2O. On stirring a benzene solution of this product (**7**) with lead dioxide for a few minutes at room temperature, the radical **5** was regenerated.

4,4,5,5-Tetramethylimidazolidin-2-one-1-oxyl (9).—Several milligrams of 1-hydroxy-4,4,5,5-tetramethylimidazolidinone (**4**) dissolved in methylene chloride were shaken with aqueous sodium periodate solution. The yellow organic layer, after drying over $MgSO_4$ displayed a strong characteristic esr spectrum of the radical $a_{N(1)}$ 10.15 G, $a_{N(3)}$ 1.60, a_H 1.65. (For coupling in water, see Table II.) In alkaline solutions the proton coupling disappeared (Figure 1a and 1b).

Alternatively, solutions of **9** could be prepared by stirring solutions of **4** with lead dioxide or by heating 2-bromo-4,4,5,5-tetramthylimidazolidine-1-oxyl (**2**, R = Br) in base, as described above, followed by neutralization with acetic or hydrochloric acid. The radical decomposed on attempted isolation.

2-Methoxy-4,4,5,5-tetramethylimidazoline-1-oxyl (2, R = OCH_3). A.—To 0.11 g of 2-bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) dissolved in 8 ml of methanol was added 0.10 g of sodium methoxide. After 1 hr the solvent was removed *in vacuo* and the residue was chromatographed on silica gel with ether to yield 0.052 g (62%) of the crystalline product. The sample was purified by recrystallization from ether–chloroform.

B.—A methanol solution containing 0.16 g of sodium methoxide and 0.30 g of 4,4,5,5-tetramethylimidazolidine-1-oxyl (**2**, R = H) was boiled for 40 min. The solution was then neutralized with 1 *N* HCl and evaporated to dryness *in vacuo*. Chromatography on silica gel with ether–chloroform gave 93 mg (26%) of the nearly pure radical.

2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (2, R = Br).[21]—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (**1**, R = Br)[3b] (5 g) was dissolved in 200 ml of dimethylformamide and stirred at room temperature with 20 g of solid sodium nitrite. The color almost immediately turned from purple to orange without addition of acid. The solid sodium nitrite was filtered off and 500 ml of benzene was added to the filtrate. After stirring for 4 min with 50 g of lead dioxide, the solution was filtered and concentrated *in vacuo*. The orange solution was diluted with 700 ml of water and extracted with benzene. Removal of the benzene *in vacuo* and chromatography of the residue on silica gel with ether gave 3.73 g (80%) of the product.

2-Amino-4,4,5,5-tetramethylimidazoline-1-oxyl (2, R = NH_2).—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) (1.0 g) was heated at reflux in 100 ml of ammonium hydroxide while bubbling ammonia gas into the solution. The solution was heated for 5 hr, cooled, partially concentrated *in vacuo*, and then stirred for 15 min with 20 g of lead dioxide. After filtration

(21) We thank Dr. D. G. B. Boocock for the preparation of this compound.

through Celite and extraction of the solution with five 50-ml portions of methylene chloride, the combined organic phase was dried and evaporated *in vacuo*. The semicrystalline residue recrystallized from hexane to give 500 mg (70%) of the nearly pure product.

This compound displayed the following absorption maxima: λ_{H_2O} (pH 8) 232 mμ (ε 4200), 451 (1050); λ_{H_2O} (pH 1) 233 mμ (ε 3920), 383 (1070); λ_{DMSO} (KO-*tert*-bu) 668 mμ (ε 590).

2-Dimethylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [2, R = $N(CH_3)_2$].—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) (500 mg) was heated under gentle reflux with 20 ml of 40% aqueous dimethylamine. After 90 min the solution was almost colorless. Most of the excess amine was removed by evaporation *in vacuo* and the residual solution was reoxidized by stirring for 15 min with 10 g of PbO_2. After filtration through Celite and extraction with three 50-ml portions of CH_2Cl_2, the combined extracts were dried over Na_2SO_4 and evaporated to leave 230 mg of the brown liquid radical. An analytical sample was obtained by molecular distillation at 0.05 mm.

This compound displayed absorption maxima at: λ_{H_2O} (pH 8) 246 mμ (ε 4200), 475 (600); λ_{H_2O} (pH 1) 244 mμ (ε 3800), 427 (900).

2-Isopropylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [2, R = $NHCH(CH_3)_2$].—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) (250 mg) dissolved in 25 ml of isopropylamine and 25 ml of water were heated under gentle reflux (55–60°) for 4 hr. The almost colorless solution showed only a very weak esr signal. After cooling to room temperature the solution was concentrated *in vacuo* and then stirred for a few minutes with 10 g of PbO_2. The solution was filtered through Celite and the filtrate extracted with five 50-ml portions of CH_2Cl_2. The combined organic phases were dried and evaporated *in vacuo* to leave a brown oil. Chromatography of this residue on silica gel with ether yielded 100 mg (44%) of the pure radical.

This compound displayed absorption maxima at: λ_{H_2O} (pH 8) 233 mμ (ε 5250), 268 (sh) (2200), 480 (1020); λ_{H_2O} (pH 1) 235 mμ (ε 5670), 270 (sh) (1970), 401 (1270); λ_{DMSO} (KO-*tert*-bu) 698 mμ (ε 430).

2-Amino-1-hydroxy-4,4,5,5-tetramethylimidazoline (17, R = NH_2).—2-Amino-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = NH_2) (70 mg) in 50 ml of methanol containing 5 mg of platinum oxide was stirred under a hydrogen atmosphere at room temperature until the solution became colorless. It was then filtered through Celite and evaporated *in vacuo*. The slightly yellow residue was recrystallized from methanol–acetone to give 20 mg of the product, mp 141–144°. The compound reoxidized slowly to the starting radical on standing in air. A satisfactory analysis was not obtained.

2-Dimethylamino-1-hydroxy-4,4,5,5-tetramethylimidazoline [17, R = $N(CH_3)_2$].—2-Dimethylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [**2**, R = $N(CH_3)_2$] (50 mg) in 50 ml of methanol containing 5 mg of platinum oxide was stirred under a hydrogen atmosphere at room temperature until the solution became colorless. The solution was then rapidly filtered through Celite and evaporated *in vacuo*. The residue was recrystallized from acetone to give 15 mg of product (sublimes without melting above 190°). The compound displayed characteristic infrared absorption at ν_{KBr} 3100 (OH) and 1605 cm^{-1} (C=N).

Anal. Calcd for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.68. Found: C, 58.33; H, 10.27; N, 22.47.

2-Cyano-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl (2, R = CN).—A finely ground mixture of 300 mg of sodium cyanide and 300 mg of 2-bromo-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide[3b] was heated in 3 ml of dry dimethylformamide at 70° for 15 min. The solution was then diluted with ether, filtered, and evaporated *in vacuo*. The residue was purified by preparative tlc (silica gel–ether) to give 66 mg (31%) of the radical.

Registry No.—**2** (R = NH_2), 26682-07-5; **2** [R = $N(CH_3)_2$], 26682-08-6; **2** [R = $NHCH(CH_3)_2$], 26682-09-7; **2** (R = OCH_3), 26682-10-0; **2** [R = $C(CH_3)_3$], 26682-11-1; **2** (R = CH_3), 26682-12-2; **2** [R = $CH_2CH(CH_3)_3$], 26682-13-3; **2** [R = $CH(CH_3)_2$], 26682-14-4; **2** (R = C_6H_5), 26731-64-6; **2** (R = H), 26682-15-5; **2** (R = I), 26682-16-6; **2** (R = Br), 26682-17-7; **2** (R = $COOCH_3$), 26682-18-8; **2** (R = C≡N), 26682-19-9; **4**, 26682-20-2; **5**, 26682-21-3; **9**, 26682-22-4; **17** (R = NH_2), 26682-23-5; **17** [R = $N(CH_3)_2$], 26682-24-6; **17b** (R = C_6H_5), 18390-03-0.

Iminophosphoranes from the Reaction of Ylides with Nitriles

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Received July 24, 1970

Benzonitrile and α-(triphenylphosphoranylidene)toluene react to give the stable iminophosphorane α-[(triphenylphosphoranylidene)amino]stilbene (**3**) which was also prepared by reaction of *cis*- or *trans*-α-azidostilbene with triphenylphosphine. A wide variety of resonance-stabilized phosphoranes and iminophosphoranes, while not reacting with unactivated nitriles, undergo the analogous reaction with cyanogen and trifluoroacetonitrile. The resulting iminophosphoranes (*e.g.*, **4** and **20**) are air stable and quite resistant to hydrolysis. Two isomers are formed in a number of cases. The reaction of nitriles with phosphoranes is believed to proceed by a mechanism analogous to that of the reaction of phosphoranes with activated acetylenes.

Part A

The nucleophilic character of phosphorus ylides has long been recognized and reactions of this class of compounds with a wide variety of electrophilic reagents have been reported.[1] Among these, however, reactions with nitriles have received less attention. McEwen and coworkers[2] found that nonresonance-stabilized ylides[1a,b] react with aliphatic and aromatic nitriles to give ketones after hydrolysis of the unidentified intermediates. We have isolated and characterized the intermediate in one such case and extended the scope to include reactions between resonance-stabilized[1a,b] ylides and the activated nitriles, cyanogen and trifluoroacetonitrile.

α-(Triphenylphosphoranylidene)toluene and benzonitrile reacted slowly in refluxing ether–benzene to give a 1:1 adduct in 68% yield. It was identified as α-[(triphenylphosphoranylidene)amino]stilbene (**3**) by independent synthesis from triphenylphosphine and either *cis*- or *trans*-α-azidostilbene. On hydrolysis, **3** gave deoxybenzoin and triphenylphosphine oxide as reported previously.[2] Attempts to add nitriles to resonance-stabilized ylides, *i.e.*, those carrying electron-withdrawing groups on the ylide carbon, were unsuccessful. How-

(1) (a) A. Maercker, *Org. React.*, **14**, 270 (1965); (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; (c) H. J. Bestmann, *Angew. Chem.*, **77**, 850 (1965), and preceding reviews.

(2) (a) R. G. Barnhardt, Jr., and W. E. McEwen, *J. Amer. Chem. Soc.*, **89**, 7009 (1967); (b) A. Bladé-Font, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **82**, 2646 (1960); (c) A. Bladé-Font, Ph.D. Thesis, University of Kansas, 1960.