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4-Phenyl-4*H*-1,2,4-triazoline-3,5-dione, an Efficient Spin Trap for Carbon- and Metal-Centered Radicals

Angelo Alberti* and Gian Franco Pedulli*†

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, CNR, 40064 Ozzano Emilia, Italy

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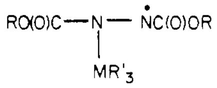
The spin adducts between a variety of organic or organometallic radicals and 4-phenyl-4*H*-1,2,4-triazoline-3,5-dione (Ph-TAD) have been investigated by ESR spectroscopy. Because of its reactivity toward metal-centered radicals which do not easily add to nitroso derivatives or nitrones, Ph-TAD can provide a valuable alternative to these more popular radical scavengers. The ambiguity present in the literature about the ESR parameters of some of the resulting 4-phenylurazolyl radicals is discussed.

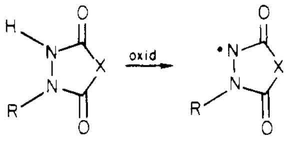
Arylhydrazyl radicals are generally rather long-lived paramagnetic species, the most striking example being diphenylpicrylhydrazyl (DPPH). Their persistency arises partly from the possibility of delocalizing the unpaired electron onto the aromatic rings and partly from the steric hindrance about the radical center. It is, however, possible to observe hydrazyl itself ($H\dot{N}NH_2$)[1] as well as mono-,[1] di-,[2] and trialkylhydrazyl radicals[2] under continuous UV irradiation of the parent hydrazines in the presence of di-*tert*-butyl peroxide (DTBP). Hydrazyls (1) having an alkylcarboxy group bonded to each nitrogen atom[3] have also been reported. These have been obtained by reaction of a number of photochemically generated carbon-centered[3a,b] or group 4B metal-centered radicals[3b] to azodicarboxylates and are characterized by half-life times of the order of a few seconds or less.



$$RO(O)C-\underset{\underset{MR'_3}{|}}{N}-\dot{N}C(O)OR$$

1, M = C, Si, Ge, Sn

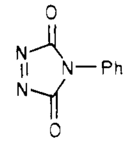
Recently it has been shown that also some hydrazyls lacking a directly bonded aromatic group may be fairly persistent. These include the radicals obtained by oxidation of urazoles (2),[4] pyrazolidinediones (3),[4] and oxadiazolidinediones (4),[5] where R is an alkyl group. The detection of 4-phenylurazolyl (R = H) has also been claimed by two groups of authors;[6a,b] however, disagreement exists concerning the ESR spectral parameters of this species.



2, X = NR′
3, X = CR′$_2$
4, X = O

The persistency of radicals 2–4 is possibly to be associated with steric crowding in the region of the two hydrazylic nitrogen atoms, as the radicals containing the bulkier R substituents are the more stable. An important role, however, is also played by the imidic nitrogen in (2) which eases up the delocalization of the unpaired electron over the molecular framework, thus rendering these species longer lived than their analogues 3 and 4.[4]

In view of the persistency of radicals 2, 4-phenyl-4*H*-1,2,4-triazoline-3,5-dione (5, Ph-TAD) would be expected to behave as a good radical scavenger, the addition of free radicals to its N=N double bond leading to substituted urazolyl radicals.

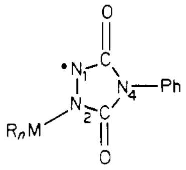


5 (Ph-TAD)

We report that Ph-TAD indeed reacts with a variety of different radicals, giving rise to spin adducts which can be readily observed and identified by means of ESR spectroscopy. In fact, the title compound has proved to be a particularly efficient spin trap for metal-centered radicals and in several cases can represent a good, commercially available substitute to nitroso derivatives or nitrones.

Results

The investigated radicals can be represented with the general structure 6, where M is a proton, a carbon, a sulfur, or a metal atom (Si, Ge, Sn, Pb, Hg, Mn, Re), and R_n are alkyls or aryls (or CO groups when M = Mn or Re). The hyperfine splitting constants and *g* factors for radical adducts **6a–s** and for the radical anion of Ph-TAD (**6t**) are collected in Table I.



6

All the ESR spectra are characterized by the interaction of the unpaired electron with three different nuclei having nuclear spin quantum number $I = 1$, one of them being much less coupled than the other two. These are clearly identifiable as the three nitrogen atoms N_1, N_2, and N_4, the latter showing the smaller coupling (see Discussion).

Thus, ESR spectra consisting of 27 lines were recorded when Ph-TAD was reacted with carbon-centered radicals having no α-hydrogen atoms, such as cumyl and butyro-

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† On leave from the Istituto Chimico dell'Università, 09100 Cagliari, Italy.

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

(2) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6110. Lunazzi, L.; Ingold, K. U. *Ibid.* **1974**, *96*, 5558.

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Table I. ESR Parameters for Radical Adducts **6a–s** and for the Radical Anion of 4-Phenylurazole (**6t**)

radical	solvent[b]	MR_n	a_{N1}	a_{N2}	a_{N1}/a_{N2}	a_{N4}	a_{other}	g	temp, K
6a	B	CH_3	7.60	5.88	1.29	1.45	7.60 (3 H)	2.0044	298
6b	toluene	CH_2Ph	7.83	5.75	1.36	1.44	4.26 (2 H)	2.0044	300
6c	B	$CHMe_2$	7.69	5.98	1.29	1.47	2.82 (1 H)	2.0044	300
6d	B	$CHPh_2$	7.90	5.88	1.34	1.46	1.46 (1 H)	2.0044	300
6e	cumene	CMe_2Ph	7.75	6.33	1.22	1.46		2.0044	294
6f	B	CMe_2CN	8.39	5.87	1.43	1.40		2.0043	302
6g	methylcyclohexane	1-methylcyclohexyl	7.64	6.21	1.23	1.47	0.37 (3 H)	2.0044	298
6h	BB	1-adamantyl	7.57	6.07	1.24	1.48	0.52 (3 H)	2.0044	300
6i	B	Ph	7.22[a]	5.65[a]	1.28	1.34	0.6 (2 H), 1.44 (2 H), 1.53 (1 H)	2.0043	348
6j	B	SPh	8.52	5.95	1.43	1.31		2.0042	353
6k	B	$SiPh_3$	8.53	4.02	2.12	1.31		2.0044	303
6l	B	$GePh_3$	8.19	4.90	1.67	1.39		2.0043	301
6m	CH_2Cl_2	$SnBu_3$	7.36	5.13	1.43	1.48	8.24 ($^{117-119}Sn$)	2.0042	293
6n	CH_2Cl_2	$PbPh_3$	7.09	5.53	1.28	1.52	6.00 (^{207}Pb)	2.0042	292
6o	B	HgPh	7.53	5.36	1.40	1.45	25.90 (^{199}Hg)	2.0043	300
6p	CH_2Cl_2	$Mn(CO)_5$	6.21	6.21	1.00	1.57	5.95 (^{53}Mn)	2.0038	297
6q	CH_2Cl_2	$Re(CO)_5$	6.42	6.07	1.06	1.54	24.86 (^{185}Re), 25.10 (^{187}Re)	2.0052	295
6r	B/HMPTA	H	8.06	4.73	1.68	1.44	6.59 (1 H)	2.0044	298
6s	B/HMPTA/D_2O	D	8.09	4.63	1.74	1.45	1.05 (1 D)	2.0044	303
6t	Me_2SO		4.78	4.78	1.00	1.76	3.46 (^{13}C)	2.0044	298

[a] Determined by computer simulation. [b] B = benzene; BB = *tert*-butylbenzene.

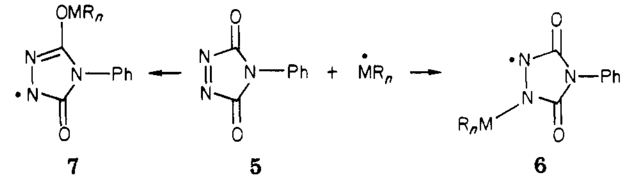
nitryl, with phenylthiyl, or with organometallic radicals where the most abundant isotope of the metal atom has no nuclear spin, like triphenylsilyl, triphenylgermyl, tributylstannyl, triphenylplumbyl, and phenylmercuryl. In the latter three cases satellite lines were detected on the two wings of the main spectrum, originating from the coupling of the unpaired electron with the less abundant metal isotopes possessing spin. With mercury (see Figure 1b) we have been able to observe two satellite spectra at lower and higher field with respect to the main signal, which can be assigned to ^{199}Hg ($I = 1/2$, na = 16.8%) while the lines due to ^{201}Hg ($I = 3/2$, na = 13.24%) were lacking. Our failure to detect ^{201}Hg satellites is consistent with previous reports[7] on mercury-containing radicals and can be possibly attributed to quadrupolar relaxation.

In the spectrum of 4-phenylurazolyl (**6r**) the basic 27-line pattern is further split into two by the hyperfine interaction with the NH proton. This doublet becomes a 1:1:1 triplet upon substitution of deuterium for the hydrogen atom.

The spectrum of the manganese pentacarbonyl adduct (**6p**) shows the coupling of the unpaired electron with the ^{55}Mn nucleus ($I = 5/2$, na = 100%), while that of the rhenium carbonyl analogue (**6q**) consists of the superposition of two spectra (see Figure 1a) originating from the coupling with the two isotopes ^{187}Re ($I = 5/2$, na = 62.93%) and ^{185}Re ($I = 5/2$, na = 37.03%). The latter organometallic radicals could be easily obtained by irradiating for a few seconds the appropriate solutions (see the Experimental Section) and were found to be very persistent, as the intensity of the ESR signal remained practically unchanged for several days.

Additional splittings were also observed in the ESR spectra of the adducts with alkyl radicals containing α-hydrogen atoms (**6a–d**), i.e., a 1:3:3:1 quartet for $MR_n = CH_3$, a 1:2:1 triplet for $MR_n = CH_2Ph$, and a doublet for $MR_n = CHMe_2$ (see Figure 2) or $CHPh_2$. A small 1:3:3:1 quartet splitting could be resolved in the spectra of **6g** and **6h**. This is probably due to the methyl protons of the 1-methylcyclohexyl substituent in the former radical and to the three bridgehead hydrogens of the 1-adamantyl group in the latter. The phenyl adduct (**6i**) of Ph-TAD gives the more complex spectrum because of the resolvable hyperfine coupling with ortho, meta, and para protons of the entering group.

Scheme I



Ph-TAD reacted spontaneously at room temperature with triphenylborine, leading to the phenyl adduct **6i** as the only observable radical species. Thermal or photolytic reaction with triphenylarsine or triphenylstibine led to radical **6r** through a mechanism as yet to be unraveled. Phosphines, pyrophosphites, and cobalt octacarbonyl reacted exothermally with Ph-TAD upon simple mixing in *tert*-butylbenzene without producing any detectable paramagnetic species.

Discussion

Nature of the Spin Adducts. In principle Ph-TAD could undergo radical addition at two different molecular sites, i.e., at the N=N double bond or at either of the two carbonyl groups according to Scheme I. In the former case diacylhydrazyl radicals **6** would be formed whereas in the latter the reaction would lead to hydrazonyl radicals of type **7**. Both kinds of reaction do actually take place in the addition of group 4B organometallic radicals to the structurally related maleimide, maleic anhydride, and maleic thioanhydride,[8] the process being kinetically controlled at lower temperatures (addition to C=C double bond favored) and thermodynamically controlled at higher temperatures (addition to the carbonyl groups favored).

On the contrary, the reaction of Ph-TAD with 18 different carbon- or metal-centered radicals always resulted in the formation of a single paramagnetic species whose ESR parameters were indicative of a hydrazyl-like structure.

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(7) Helbert, J. N.; Kopf, P. W.; Poindexter, E. H.; Wagner, B. E. *J. Chem. Soc., Dalton Trans.* **1975**, 998.

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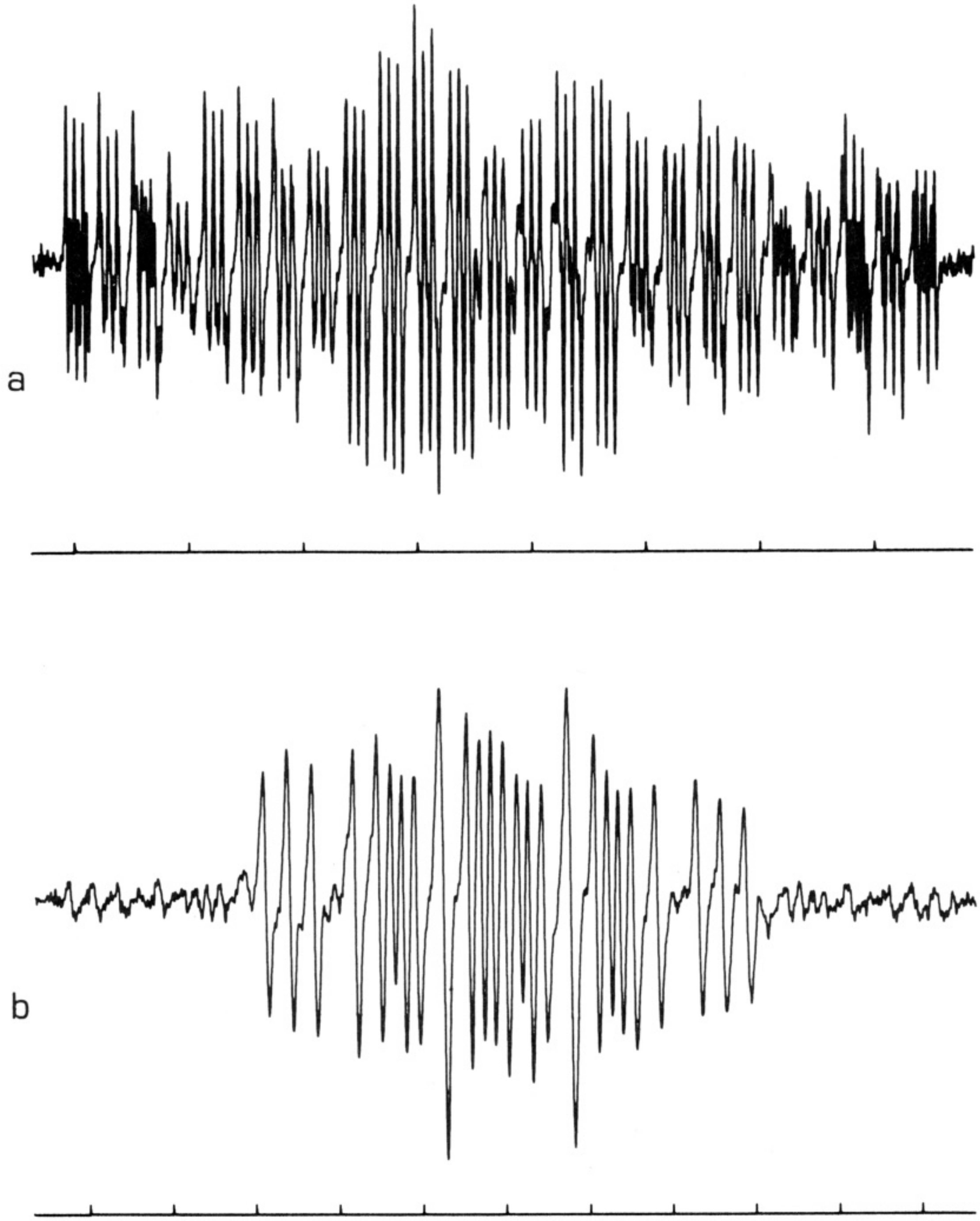

Figure 1. (a) Room-temperature ESR spectrum of radical **6q** in methylene chloride (spacing marks 20 G). (b) ESR spectrum of radical **6o** at 343 K in benzene (spacing marks 5 G).

Further evidence that the reaction really follows the pathway leading to spin adducts **6** is provided by the consistency of the ESR parameters for the adducts resulting from addition of phenyl (**6i**) or cumyl (**6e**) to Ph-TAD with those of the radicals obtained by Pirkle and Gravel by oxidation of the correspondingly substituted urazoles.[4]

Radicals of general structure **6** are found to be rather stable, especially when no hydrogens are bonded to the hydrazylic nitrogen or to the M atom of the entering MR_n group. In fact, thermolysis or photolysis of Ph-TAD with the proper reactants (see Experimental Section) gives rise to intense and well-resolved ESR spectra due to radicals **6a–s**. However, if the photolysis is interrupted or the temperature is lowered, the signals due to radicals **6a–d** and **6r–s** decay in a time interval ranging from few seconds to several minutes. Actually it is known that radicals **2–4** can give a reversible dimerization, the equilibrium being shifted at room temperature toward the dimers.[4,6b] A higher persistency is instead shown by all the other radicals which can be detected over long time intervals at room temperature in the absence of UV irradiation. This is especially so for the organometallic radicals **6m–q**, the more persistent being the $Mn(CO)_5$ and $Re(CO)_5$ derivatives **6p** and **6q**, which are characterized by half-life times of many days.

The high efficiency of Ph-TAD as a spin trap for many metal-centered radicals and the remarkable persistency of the resulting adducts are very interesting in view of the low reactivity of group 4B organometallic radicals toward the most commonly used scavengers, such as nitroso derivatives and nitrones to give the corresponding nitroxides,[9]

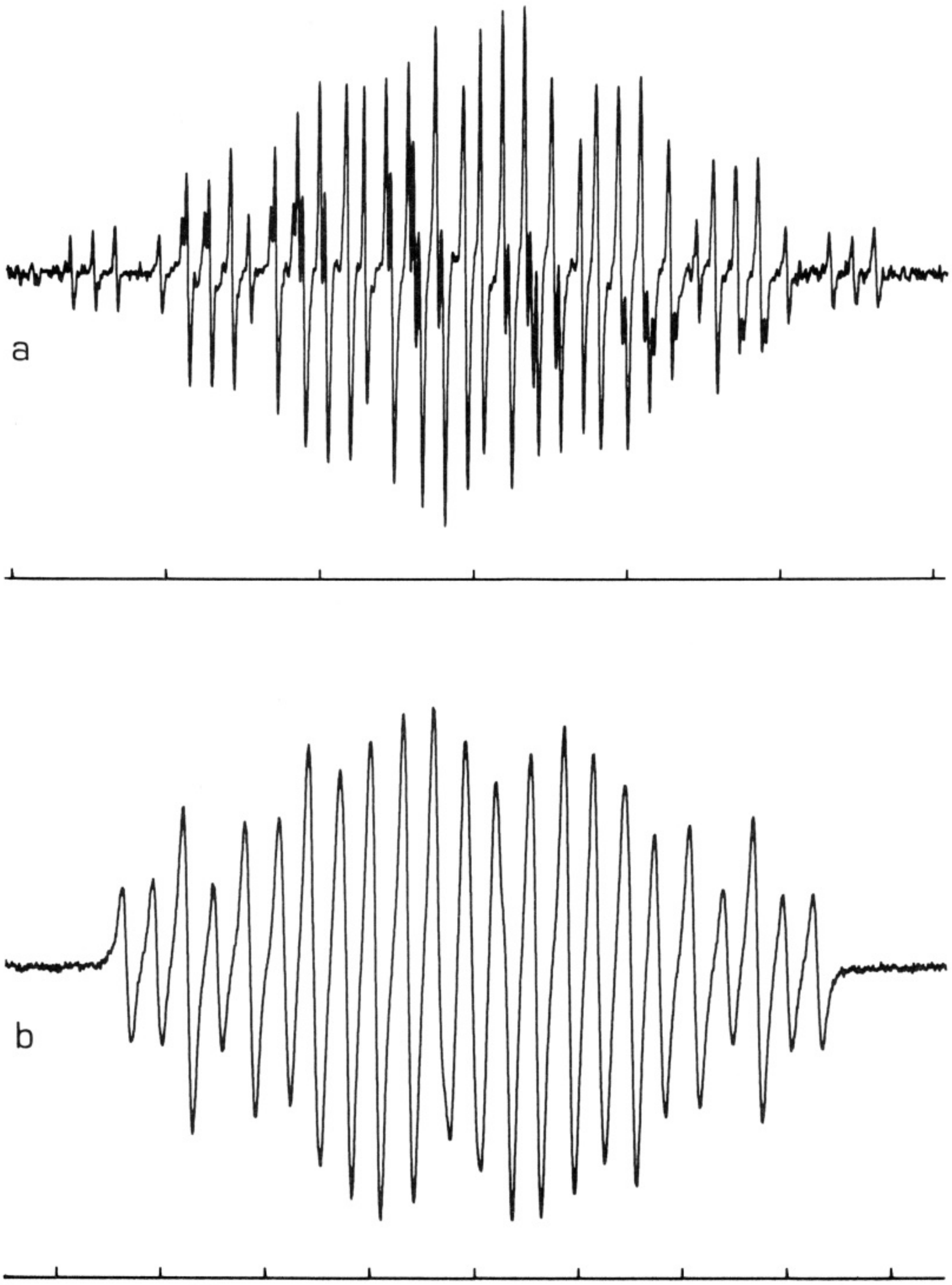

Figure 2. (a) Room-temperature ESR spectrum of radical **6a** in benzene (spacing marks 10 G). (b) Room-temperature ESR spectrum of radical **6c** in benzene (spacing marks 5 G).

and of the rather low stability of nitroxides containing a manganese or rhenium atom directly bound to the nitrogen nucleus.[10] Spin adducts **6** can be considered as *captodative*-stabilized radicals,[11] the electron acceptor being the carbonyl group and the electron donor being the trivalent hydrazylic nitrogen. Since the donating effect of the latter becomes stronger with the increasing metallic character of the M atom of the linked MR_n group, a parallel increase in the stability of the resulting radical adduct is consequently expected. On this basis we believe that Ph-TAD can represent a valuable and easily available substitute for the above-mentioned radical scavengers in those cases when they prove ineffectual.

Radical **6r**, i.e., 4-phenylurazolyl, deserves a special comment because contradictory data concerning this species have appeared in the literature. The first observation of this radical was reported in 1977 by Wamhoff and Wald,[6] who assigned to **6r** the following set of hyperfine splitting constants: $a_{N1(2)} = 8.4$ G, $a_{N2(1)} = 6.8$ G, $a_{N4} = 1.4$ G, $a_H = 4.8$ G. Actually it would appear that the values of $a_{N2(1)}$ and a_H need interchanging as follows: $a_{N1(2)}$

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[9] Camaggi, C. M.; Caser, M.; Guerra, M.; Placucci, G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1675.

[10] Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans. 2* **1977**, 551. Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1980**, *194*, 343.

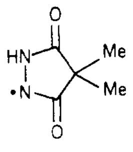
[11] Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

= 8.4 G, $a_{N2(1)}$ = 4.8 G, a_{N4} = 1.4 G, and a_H = 6.8 G, this new set of parameters accounting nicely for both their experimental and simulated spectra. Wamhoff and Wald's assignment, however, remained unchallenged until very recently, when Hall and co-workers[6b] reported the detection of an ESR spectrum interpreted in terms of the following couplings: a_{N1} = 7.64 G, a_{N2} = 6.21 G, a_{N4} = 1.50 G, and a_H = 3.01 G, which the authors assigned to the authentic 4-phenylurazolyl, leaving the nature of Wamhoff and Wald's radical open to speculation.

Accordingly, in the course of the present study, we dissolved different samples of commercially available Ph-TAD (Fluka) in a number of solvents at room temperature, but we could not detect any ESR signal. We subsequently tried to generate 4-phenylurazolyl by means of a procedure that had already proved successful in other cases,[8,12] i.e., by photolyzing a solution similar to those used for generating the silyl or germyl adducts **6k** and **6j** to which a few drops of hexamethylphosphoric triamide (HMPTA) had been added. The resulting intense and well-resolved spectrum was very similar to that reported by Wamhoff and Wald. It was characterized by rather narrow lines, as should be expected for the hydrogen adduct, and could be perfectly matched by using the parameters reported in Table I for **6r**.

In order to check whether the 6.59-G doublet splitting was actually due to a hydrazylic proton, we added to the sample a few drops of D_2O. This led to the instantaneous disappearance of the original spectrum which was replaced by a new one where the 6.59-G doublet had changed into a 1.05-G 1:1:1 triplet attributable to a deuterium atom (according to the proton–deuterium moment ratio the expected splitting is 1.01 G).

We are aware that a 6.59-G splitting can appear to be rather large for a hydrazylic hydrogen if compared to the values measured in other hydrazyls;[1] on the other hand, a_H^{NH} splittings of protons bound to a trivalent nitrogen atom have been found in other radicals, as for instance pyridinyls,[13] to be strongly dependent on the nature of the substituent. Thus electron withdrawing substituents such as carbonyls or cyano groups in the 4-position of pyridinyls produce an increase of the a_H^{NH} coupling. This behavior has been explained in terms of a change of the average configuration at the nitrogen atom from slightly pyramidal to planar, due to a stabilization of resonant structures with the nitrogen bearing a formal positive charge.[13] A similar interpretation may also hold in the present case, and thus the large a_H^{NH} splitting measured in **6r** may be taken as an indication of the greater planarity of the trivalent nitrogen in urazolyls with respect to alkylhydrazyls. Actually, also in the structurally related hydrazyl **8**, generated by Roberts and Winter[3b] by hydrogen abstraction from the parent hydrazine (a_{N1} = 8.8 G, a_{N2} = 4.6 G, a_H = 7.4 G), the proton splitting is of the same order of magnitude as for radical **6r**. Therefore, we feel confident that the paramagnetic species produced by the procedure described above is indeed the 4-phenylurazolyl radical **6r** and believe that it is the same species observed by Wamhoff and Wald, whose spectrum had been apparently misinterpreted.



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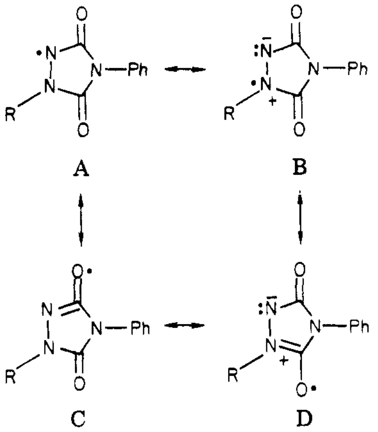
Scheme II



We cannot avoid noticing that the spectral pattern and hyperfine couplings observed by Hall et al. and assigned to 4-phenylurazolyl are not dissimilar from those exhibited by our isopropyl-substituted radical (**6c**; see Table I and Figure 2b). This suggests that the spectrum obtained by these authors is in fact due to a spin adduct between Ph-TAD and a carbon-centered radical bearing an α-hydrogen atom.

Spin Density Distribution. The most relevant mesomeric structures which can be envisaged to represent radicals **6** are depicted in Scheme II. Accordingly, most of the spin density in these species may be localized on the nitrogens N_I and N_2 and on the oxygens of the adjacent carbonyl groups. Consequently, the smaller coupling (1.3–1.5 G) can be safely assigned to the imidic nitrogen N_4, the insensitivity of this splitting to the nature of the substituent R being due to the insulating effect of the two carbonyl groups. An unambiguous assignment of the other two coupling constants would require labeling of either N_1 or N_2. Ingold et al. in their studies of some mono-, di-, and trialkyl ^{15}N-labeled hydrazyls have shown that the divalent nitrogen may or may not be responsible for the larger splitting depending on the numer and position of the substituents.[2]

Pirkle and Gravel[4,5] assigned the larger splitting to the divalent nitrogen of urazolyls by similarity with DPPH. A more pertinent comparison should be made with the radicals of general structure **1** obtained by radical addition to dialkylazodicarboxylates. A number of these species have been investigated by Roberts and Winter,[3b] and they too stress the necessity of ^{15}N labeling to unambiguously assess which nitrogen atom is responsible for which coupling. However, these authors note that in the silicon-, germanium-, and tin-containing hydrazyls (**1**) a marked decrease of the larger nitrogen splitting was observable when going from the lighter to the heavier group 4B substituents which was paralleled by an increase of the smaller nitrogen coupling. Thus, on the ground that "... the relative importance of E, and hence the value a_{N1}/a_{N2}, should

$$\underset{\mathrm{E}}{\mathrm{RO_2C(Ph_3M)N^2{-}\dot{N}^1{-}CO_2R}} \leftrightarrow$$

$$\underset{\mathrm{F}}{\mathrm{RO_2C(Ph_3M)\dot{N}^{2+}{-}N^{1-}{-}CO_2R}}$$

increase with the π-acceptor character of M in the order Sn < Ge < Si ..." Roberts and Winter tentatively assigned the larger coupling constants to N_1.

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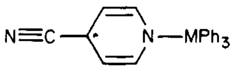
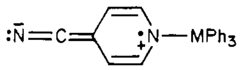
[12] Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1979**, *164*, 219. Alberti, A.; Martelli, G.; Hudson, A.; Pedulli, G. F.; Tiecco, M.; Ciminale, F. *Ibid.* **1979**, *182*, 333.

[13] Guerra, M.; Bernardi, F.; Pedulli, G. F. *Chem. Phys. Lett.* **1977**, *48*, 311. Alberta, A.; Guerra, M.; Pedulli, G. F. *J. Magn. Reson.* **1979**, *34*, 233.

Resonance structures E and F are the equivalent of structures A and B, respectively, and it is not unexpected that we find for radicals **6k–n** a trend of the a_{N1} and a_{N2} couplings analogous to that reported for the similarly substituted radicals **1**. On this basis it seems to us that also in the urazolyls the divalent nitrogen should be thought to be responsible for the larger hyperfine splitting. Such an assignment gains further support from the comparison with the heterocyclic nitrogen splitting a_N of some 4-cyanopyridinyls of general formula **9**, M being a group 4B metal,[14] where the two limiting structures **9a** and **9b**, analogous to A and B for urazolyls, can be envisaged. In these radicals a_N increases along the sequence Si < Ge < Sn, following the same trend of the smaller nitrogen splitting observed in the related urazolyls, which thus can be safely assigned to the trivalent nitrogen atom. A similar behavior has also been found in the group 4B organometallic adducts of pyrazine and of some substituted benzo-2,1,3-thiadiazoles.[15]



9a



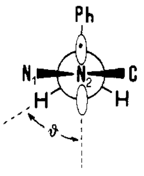
9b

Conformational Stability. In the adducts between **5** and carbon-centered radicals with two or one α-hydrogen atoms (**6b–d**), the magnitude of the isotropic hyperfine splittings at these protons allows one to establish the preferred conformation of the entering group. This can be done by means of the usual relation if sp^2 hybridization

$$a_H = A + B\langle\cos^2\vartheta\rangle$$

is assumed at the trivalent nitrogen atom (see preceeding section). Here ϑ is the dihedral angle between the symmetry axis of the 2p$_z$ orbital on N$_2$ and the C-H bond, A is usually neglected, and B is assumed to be twice the hyperfine splitting of the methyl protons in the related methyl substituted radical (**6a**, in the present case) where $\langle\cos^2\vartheta\rangle$ is 0.5 for symmetry reasons. B can therefore be taken as 15.2 G.

The benzyl radical adduct **6b** seems to adopt conformation **10**, with the phenyl group eclipsing the 2p$_z$ orbital of N$_2$, since the 4.26-G splitting of the CH$_2$ protons is very close to the value (3.8 G) predicted for a ϑ angle of 60°.



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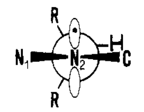

11

In the isopropyl (**6c**) and diphenylmethyl (**6d**) adducts the couplings of 1.46 and 2.82 G indicate that the C–H proton is closer to the nodal plane of the π orbital, thus suggesting preference for conformation **11** or for the one obtainable by a 180° degree rotation of **11**. The larger a_H value measured for **6c** suggests a greater torsional freedom about the equilibrium position of the isopropyl group with respect to the more bulky diphenylmethyl substituent.

Experimental Section

All chemicals were commercially available and were used without further purification. All samples were deoxygenated by bubbling dry nitrogen through the solutions. Thorough degassing of the solutions by means of the freeze–thaw technique did not result in any improvement of the quality of the ESR spectra. These were recorded on a Bruker ER 200 spectrometer equipped with a NMR gaussmeter (calibration of the field), a frequency counter (*g* factor determination), and a standard variable-temperature device; a high pressure mercury lamp (1 kW) was used as a source of UV light.

The radicals to be trapped were mostly generated by continuous UV irradiation of benzene or methylene chloride solutions of the triazoline containing small amounts of di-*tert*-butyl peroxide (DTBP) and diphenylmethane (spin adduct **6d**), adamantane (**6h**), triphenylsilane (**6k**), or triphenylgermanium hydride (**6l**). In the case of radicals **6b,e,g**, toluene, cumene, and methylcyclohexane were respectively used as solvents. No DTBP was needed in the photolysis of diacetyl peroxide (**6a**), azobis(isobutyronitrile) (**6f**), dibenzoyl peroxide (**6i**), diphenyl disulfide (**6j**), hexabutylditin (**6m**), hexaphenyldilead (**6n**), manganese decacarbonyl (**6p**), and rhenium decacarbonyl (**6q**). In the latter two cases the resulting spin adducts were very persistent, and best resolution was obtained by cutting off the UV light after 2–3 s of irradiation. Radical **6c** was generated by photolyzing a mixture of isopropyl bromide, triphenylsilane, DTBP, and Ph-TAD in butylbenzene, while the hydrogen adduct **6r** was obtained by adding some hexamethylphosphoric triamide to the solutions used to generate radicals **6k** and **6l**. Adduct **6r** could be converted into its deuterium analogue **6s** by addition of a small amount of D$_2$O.

Reduction of Ph-TAD to the corresponding radical anion **6t** was carried out with potassium *tert*-butoxide in Me$_2$SO.

Registry No. 5, 4233-33-4; **6a**, 85864-69-3; **6b**, 85864-70-6; **6c**, 85864-71-7; **6d**, 85864-72-8; **6e**, 64739-52-2; **6f**, 85864-73-9; **6g**, 85864-74-0; **6h**, 85864-75-1; **6i**, 64739-49-7; **6j**, 85864-76-2; **6k**, 85864-77-3; **6l**, 85864-78-4; **6m**, 85864-79-5; **6n**, 85864-80-8; **6o**, 85864-66-0; **6p**, 85864-67-1; **6q**, 85864-68-2; **6r**, 80540-38-1; **6s**, 85864-81-9; **6t**, 85882-53-7.

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[14] Alberti, A.; Pedulli, G. F. *Tetrahedron Lett.* **1978**, 3283.

[15] Alberti, A.; Pedulli, G. F., to be submitted for publication.