Addition of Organometallic Radicals to Organic Substrates. A Useful Spin-trap Reagent for Group 4 Radicals

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Silyl, germyl, and stannyl radicals add to the carbon–nitrogen double bond of *N*-dicyanomethyleneaniline (1) giving

$$\underset{(1)}{\mathrm{Ar{-}N{=}C(CN)_2}} + \mathrm{R_3M^{\bullet}} \longrightarrow \mathrm{Ar{-}N(MR_3){-}\dot{C}(CN)_2}$$

persistent paramagnetic species detected by e.s.r. spectroscopy. Compounds (1) are photostabile and do not give observable paramagnetic adducts with carbon- or oxygen-centred radicals; they can therefore be regarded as suitable ' spin-trap ' reagents for group 4B radicals, not easily scavenged by nitroso-derivatives.

The dicyanomethylene group has been proposed as a chemical analogue of oxygen, and compounds that differ solely in the presence of the $C(CN)_2$ component in place of an oxygen atom frequently show surprising agreement in their reactivity.[1]

Nitroso-derivatives are quite efficient radical traps; the addition of a broad range of free radicals to these compounds gives rise to stable nitroxides that can be detected by e.s.r. spectroscopy. Similar behaviour would be expected for *N*-dicyanomethyleneamines; these compounds, not available through conventional synthetic pathways, can now be prepared easily by the reaction between tetracyanoethylene and 1,3-diaryltriazenes [2] [reaction (1)].

$$\mathrm{ArN{=}N{-}NHAr} + \mathrm{(NC)_2C{=}C(CN)_2} \xrightarrow[\mathrm{Et_2O}]{\text{room temp.}} \mathrm{ArNHN{=}C(CN)_2} + \mathrm{ArN{=}C(CN)_2} \quad (1)$$

We have investigated some aspects of the homolytic reactivity of compounds (1); in addition, the well resolved e.s.r. spectra of the persistent paramagnetic adducts between (1) and silyl, germyl, and stannyl radicals have enabled us to discuss the structure of this new class of stable free radicals with emphasis on the differences between them and the corresponding nitroxides.

RESULTS AND DISCUSSION

We have generated a number of carbon-centred radicals directly in the cavity of an e.s.r. spectrometer in the presence of (1; Ar = Ph, p-Bu^{t}C$_6$H$_4$, and p-MeOC$_6$H$_4$). No persistent paramagnetic adducts were observed under conditions under which nitrosobenzene readily scavenges these species giving stable nitroxides. Photolysis experiments in addition show that compounds (1) are stable during irradiation; nitrosoarenes, in contrast, are known to decompose quickly giving diaryl nitroxides.

Different behaviour was observed when silyl, germyl, and stannyl radicals were produced from a suitable precursor. When a mixture of (1), triethyl- or triphenylsilane, and di-t-butyl peroxide in benzene was irradiated for a few seconds, an intense e.s.r. spectrum was observed (Figure 1). Analogous results were obtained with triphenylgermane and by photolysis of (1) in the presence of hexamethyl- or hexabutyl-ditin. The Table reports hyperfine splitting (h.f.s.) constants for the observed radicals; they do not decay appreciably hours after removal of the u.v. light.

The radicals in the Table are characterized by spectra with g factors of *ca.* 2.003 5, an h.f.s. from four equivalent protons (0.4—0.7 G) and two equivalent nitrogen atoms (2.0—2.15 G), and another larger nitrogen h.f.s. constant which is much more dependent on the scavenged radical.

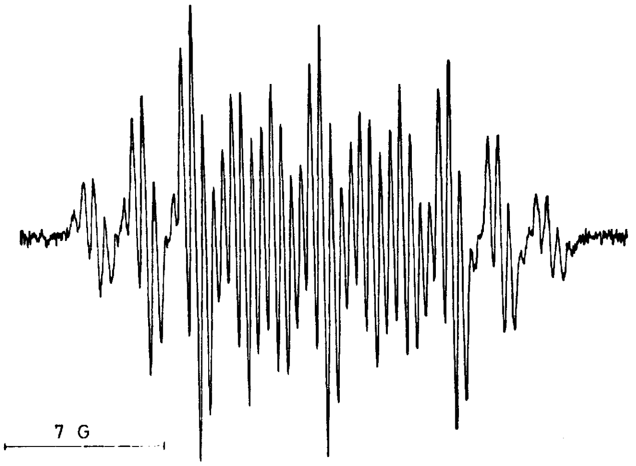
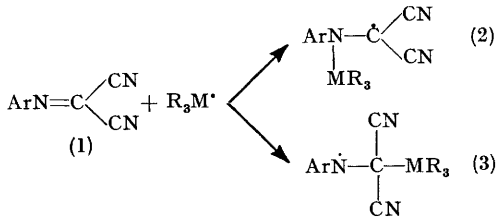


FIGURE 1 E.s.r. spectrum of p-Bu^{t}C$_6$H$_4$N(SiEt$_3$)$\dot{C}$(CN)$_2$

The aromatic proton h.f.s. constants follow a rather unusual pattern, somewhat intermediate between that typical for planar π-delocalized radicals like nitroxides, benzyls, and aminyls [a_H (*ortho*) $\geqslant a_H$(*para*) $> a_H$ (*meta*)] and that observed in σ-type radicals such as PhCO$^{\bullet}$, where the unpaired electron occupies an in-plane orbital and the largest experimental and calculated splittings derive from *meta* protons. [3]

A priori, two different radicals (2) and (3) can be obtained by addition of $^{\bullet}$MR$_3$ to (1), depending on the orientation of the reaction. E.s.r. parameters appear to be more in agreement with those expected for species (2). Although our measured g factor is quite close to that reported for PhṄBu^t,[4] other chemical as well as spectroscopic properties of the addition product are completely different. Anilino-radicals are in fact π radicals with



a_H(*para*) > a_H *ortho*) > a_H (*meta*) and are easily oxidized to nitroxides; in contrast, our adduct is stable even when generated in poorly degassed samples. This assignment is in complete agreement with theoretical predictions[5] about the preferred orientation of attack on the simplest dicyanomethyleneamine $NHC(CN)_2$. Both HOMO and LUMO coefficients are much larger on the nitrogen atom involved in the double bond than on the adjacent carbon (Figure 2).

Interactions between the singly occupied orbital (SOMO) of both electrophilic and nucleophilic radicals and the HOMO or LUMO of dicyanomethyleneamine will consequently lead to the same addition product. It is interesting that application of the same approach to the reactivity of nitroso-derivatives leads to the conclusion that both nitrogen or oxygen can be attacked by free radicals, depending on the electronic structure of the incoming species. This behaviour has actually been observed.

Simple HOMO–LUMO arguments, while giving an indication on the preferred orientation of the addition, do not explain why group 4 radicals react with dicyanomethyleneamine while carbon- and oxygen-centred radicals do not. Other authors have rationalized the analogous behaviour observed in the addition to carbon–oxygen double bonds on the basis of thermodynamic arguments.[6]

INDO M.O. Calculations reproduce well the experimental pattern of coupling constants. As the unpaired electron is mainly localized on the 2*p* π AO of C-2 (Figure 2), the extent of π-delocalization on the phenyl ring is quite small even in a planar configuration; small steric crowding around N-1 can twist the aromatic ring out of the plane, giving the observed spin-density pattern.

Hyperfine splitting constants of the radicals (2) in benzene at room temperature

−MR	$-SiPh_3$	$-SiEt_3$	$-GePh_3$	$-SnBu_3$	−H, INDO calculations [a]
Ar = Ph					
a_H (*ortho*)	*c*	0.40	0.50	0.65	−0.18 [b]
a_H (*meta*)	*c*	0.40	0.50	0.65	0.27 [b]
a_H (*para*)	*c*	0.15	0.20	*c*	−0.07
a_{CN}	2.15	2.15	2.15	2.05	3.15 [N(4)] 3.12 [N(4′)]
a_N	5.05	5.55	6.70	7.55	6.95
Ar = *p*-Bu^{t}C$_6$H$_4$					
a_H (*ortho*)	0.40	0.45	0.50	0.70	
a_H (*meta*)	0.40	0.45	0.50	0.70	
a_{CN}	2.15	2.15	2.10	2.00	
a_N	5.05	5.60	6.70	7.50	

[a] See Experimental section. [b] Average value. [c] Not resolved.

The high reactivity of *N*-dicyanomethyleneanilines towards silyl, germyl, and stannyl radicals does not parallel the behaviour of nitroso-derivatives. There are no reports available on aryl silyl nitroxides; silyl radicals are reported to attack the oxygen atom of NO and nitroso-derivatives.[7] Although in at least one instance stannyl radicals have been generated in the presence of nitroso-derivatives, no reaction between these two species was observed.[8] In contrast, nitroso-derivatives are quite reactive towards carbon- and oxygen-centred radicals that are not scavenged by (1).

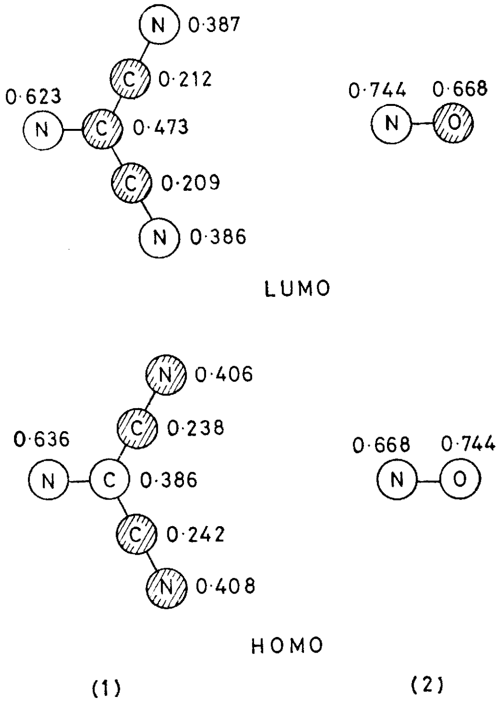
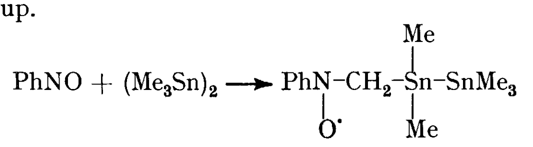


FIGURE 2 2*p*π A.O. coefficients in the HOMO and LUMO of $HN{=}C(CN)_2$ and HNO. The shading indicates the negative lobe

We carried out some experiments in order to check this behaviour. Photolysis of solutions in triethylsilane of nitrosobenzene and di-t-butyl peroxide gave only e.s.r. signals due to diphenyl nitroxide and t-butoxy phenyl nitroxide; an e.s.r. spectrum possibly due to triethylsilyl phenyl nitroxide [a_N 12.0; a_H(*ortho*) = a_H(*para*) = 1.80; a_H(*meta*) 0.90 G] was observed as a rather labile species only by photolysing very dilute solutions of nitrosobenzene in triethylsilane, without addition of di-t-butyl peroxide.

Degassed solutions in benzene of hexamethylditin and nitrosobenzene gave an intense e.s.r. spectrum even without irradiation. Spectral parameters [a_H(*ortho*) = a_H(*para*) = 2.80; a_H(*meta*) 0.95; a_N 10.90; $a(CH_2)$ 8.20] show that the observed radical is not a trialkylstannyl phenyl nitroxide, expected from the trapping of a stannyl radical by nitrosobenzene, but is the nitroxide (4) in which a $-CH_2-$ unit is directly bonded to the NO group.



$$\mathrm{PhNO} + (\mathrm{Me_3Sn})_2 \longrightarrow \mathrm{Ph}\underset{\mathrm{O^{\bullet}}}{\mathrm{N}}\mathrm{-CH_2-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Sn}}}\mathrm{-SnMe_3}$$

(4)

Figure 3 shows the observed e.s.r. spectrum for the radical (4). The reaction leading to this species, formally the insertion of a nitroso-group into a carbon-hydrogen bond followed by oxidation of the resulting hydroxylamine, may be an example of molecule-induced homolysis, and does not happen if nitrosobenzene is replaced by nitrosobutane.

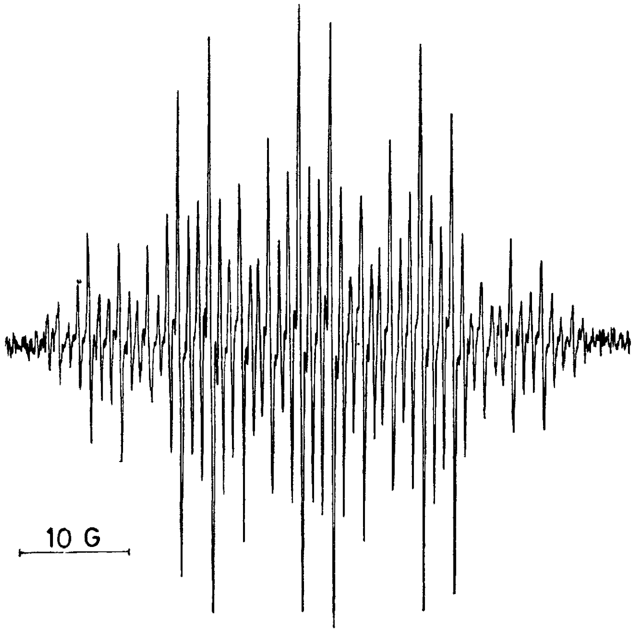
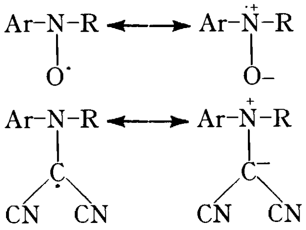


FIGURE 3 E.s.r. spectrum of (4). The inside lines are due to a small amount of diphenyl nitroxide impurity

Conclusions.—The behaviour of nitroso-derivatives and *N*-dicyanomethyleneanilines towards free radical attack seems to be quite different. Nitroso-derivatives, efficient scavengers for several organic and inorganic radicals, are surprisingly inefficient traps for the detection of silyl, stannyl, and germyl radicals. In contrast, (1) is a suitable 'spin-trap' reagent for these radicals, even in the presence of oxygen- and carbon-centred radicals that do not give persistent paramagnetic species with this substrate.



$$\mathrm{Ar-}\underset{\mathrm{O^{\bullet}}}{\mathrm{N}}\mathrm{-R} \longleftrightarrow \mathrm{Ar-}\underset{\mathrm{O^{-}}}{\overset{\cdot +}{\mathrm{N}}}\mathrm{-R}$$

$$\mathrm{Ar-}\underset{\overset{|}{\dot{\mathrm{C}}}\mathrm{(CN)_2}}{\mathrm{N}}\mathrm{-R} \longleftrightarrow \mathrm{Ar-}\underset{\overset{|}{\mathrm{C}^{-}}\mathrm{(CN)_2}}{\overset{+}{\mathrm{N}}}\mathrm{-R}$$

(2a) (2b)

The radical adduct (2) is remarkably stable and must be regarded as a stabilized carbon-centred radical (2a); the mesomeric form (2b) with the unpaired electron on a charged nitrogen, so important for the nitroxides, does not contribute much to the structure of (2).

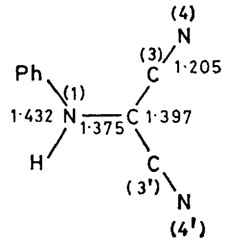
EXPERIMENTAL

N-Dicyanomethyleneanilines were synthesized as previously reported from 1,3-diaryltriazenes and tetracyanoethylene in dry ethyl ether at room temperature and separated and purified by column chromatography.

E.s.r. spectra were recorded on a VARIAN E4 instrument at room temperature; samples were degassed by nitrogen bubbling.

M.O. Calculations.—M.O. Calculations within the INDO [9] framework were carried out on $\mathrm{PhNH\dot{C}(CN)_2}$ to determine its conformational properties and hyperfine coupling constants. All the bond lengths were optimized except the N–H length which was kept fixed at 1.01 Å; standard bond angles [9] were used and the geometry of benzene was assumed for the phenyl ring.

The optimized bond lengths are shown in structure (A).



(A)

In addition, calculations show that: (i) the radical is pyramidal at N(1) with an out-of-plane angle of 26.58°; (ii) the rotation about the N(1)–C(2) bond is hindered on the e.s.r. time scale (energy barrier of 11.52 kcal mol^{-1}); (iii) in contrast the energy barrier to rotation of the phenyl ring is relatively small (0.32 kcal mol^{-1}) even without a bulky group attached to N(1); (iv) the inversion at N(1) in the conformation with the phenyl ring perpendicular to the C(Ph)–N(1)–H plane requires a smaller energy (0.44 kcal mol^{-1}) than when the ring is coplanar (8.63 kcal mol^{-1}).

These results suggest that with a bulky atom the phenyl should prefer a perpendicular conformation and N(1) should undergo a fast inversion on the e.s.r. time scale.

The last column of the Table therefore reports the hyperfine splitting constants obtained by open-shell INDO MO calculations, for the radical $\mathrm{Ph{-}NH{-}\dot{C}(CN)_2}$ in the pyramidal conformation at N(1) and with the phenyl group in a perpendicular position.

INDO calculation were also carried out on $\mathrm{H{-}N{=}C{-}(CN)_2}$ and HNO to determine the orientation of radical addition; according to Epiotis,[5] the reactivity at a particular position in a substrate is proportional to the size of the corresponding AO coefficient in the HOMO (electrophilic radical attack) and in the LUMO (nucleophilic radical attack). These M.O.s are reported in Figure 1 for both molecules.

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