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FREE RADICALS DERIVED FROM 1,4-DIAZA-1,3-BUTADIENES

I. ESR OF ADDUCTS WITH SILYL, GERMYL AND STANNYL RADICALS AND OF THE DIPROTONATED RADICAL CATION

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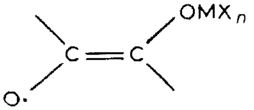
Summary

Silyl, germyl and stannyl radicals add to *N,N'*-di-t-butyl-1,4-diaza-1,3-butadiene (t-Bu-DAB) to give *cis* and *trans* isomers of 1-azaallylic radicals. Similar isomers have also been observed in the ESR spectrum of the diprotonated t-Bu-DAB radical cation.

Numerous ESR studies have been reported of free radical addition to α-diketones or *ortho*-quinones. The observed radicals are generally of type I or II. In some cases



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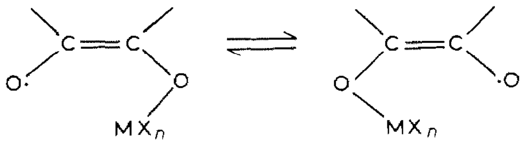

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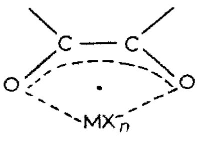

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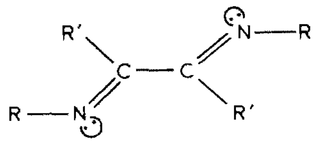

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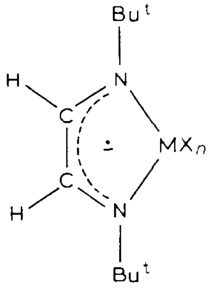
the ESR spectra exhibit temperature-dependent linewidths indicative of a dynamic equilibrium between equivalent conformers (e.g. IB). Typically the fragment MX_n involves either an element M of Group IIIB, IVB or VB where X may be alkyl, aryl or halogen (e.g. $AlEt_2$ [1], $SnCl_3$ [2], $BiPh_2$ [3]), or a transition metal carbonyl (e.g. $Re(CO)_4$, $Mn(CO)_4$ [4]). Relatively few studies have been reported of radicals derived from isoelectronic 1,4-diaza-1,3-butadienes (R-DAB), although there is currently considerable interest in the chemistry of these versatile ligands [5].

The di-t-butyl compound t-Bu-DAB (III, R = t-Bu, R′ = H) has the advantage of giving relatively simple spectra and is the system of choice for ESR studies. Zelewsky and coworkers [6] prepared the radical anion and a number of metal complexes IV where M = Zn or an alkaline earth metal. Ion-pairs with alkali metals have also been prepared [7,8]. Tom Dieck and coworkers [9] investigated the radical anions of a series of Cr, Mo and W carbonyls containing R-DAB ligands. Recently a free radical intermediate has been detected in the reaction of t-Bu-DAB with $ZnEt_2$ [10]. In these systems the ligand adopts a *cis* conformation: the free ligand is believed to exist predominantly in the S-*trans* conformation III.

We now report an investigation of the addition of Group IVB (Si, Ge, Sn) metal-centred radicals to t-Bu-DAB. We also report a spectrum which we assign to the diprotonated radical V. A subsequent publication will deal with radicals observed during the reactions of t-Bu-DAB with Group IIIB and VB compounds and with transition metal carbonyls.



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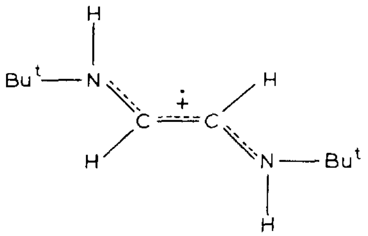

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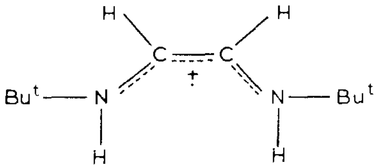


(VB)

Results

The ESR spectrum obtained by the addition of triphenylsilyl radicals to t-Bu-DAB in the range 293–373 K exhibits a slight asymmetry at low temperatures but at high

(*Continued on p. 317*)

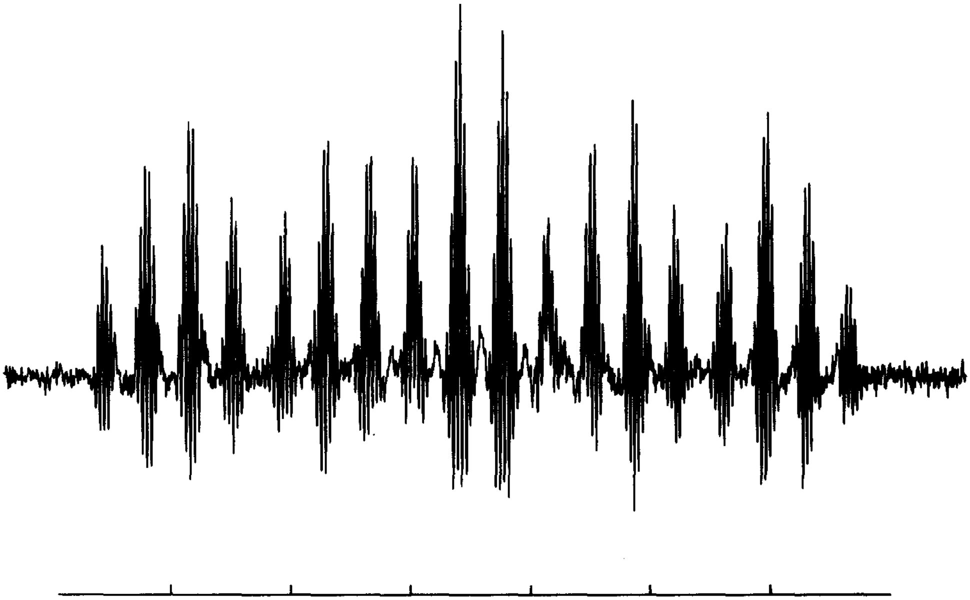


Fig. 1. 2nd derivative ESR spectrum of radical VI ($X = SiPh_3$) and t-butylbenzene/di-t-butylperoxide at 363 K. Marks at 5.0 G intervals.

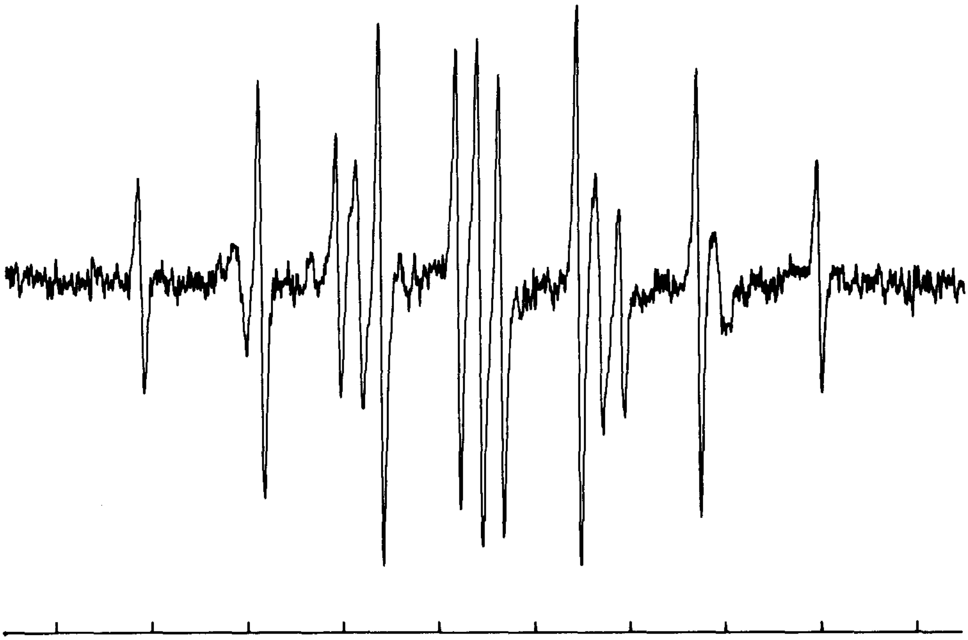


Fig. 2. ESR spectrum of Radical VI ($X = SnPh_3$) in t-butylbenzene/di-t-butylperoxide at 373 K. Marks at 5.0 G intervals.

TABLE 1

HYPERFINE COUPLING CONSTANTS (GAUSS) FOR RADICAL ADDUCTS (VI) AND THE CATION RADICAL (V)

R	X		$a(N_1)$	$a(H_2)$	$a(H_3)$	$a(N_4)$	$a(R)$	g	T (K)
t-Bu	$SiPh_3$		7.44	1.79	11.23	1.79	0.18	2.0034	373
t-Bu	$GePh_3$	A	6.94	0.37	10.11	3.45	–	2.0036	343
		B	7.46	1.01	9.83	1.79	not resol.	2.0034	343
t-Bu	$SnPh_3$ [a]		6.20	5.15	5.15	6.20	–	2.0028	353
t-Bu	$SnPh_3(C_6H_6)$		6.16	4.12	4.12	6.16	–	2.0030	298
	(THF)		7.34	4.9	4.9	7.34	–	2.0031	298
i-Pr	$GePh_3$		11.2	–	10.32	–	6.25 [b]	2.0035	298
			7.28	–	10.66	–	4.29 [b], 7.93 [b]	2.0035	298
i-Pr	$SnPh_3$ [d]		5.68	5.68	5.68	5.68	2.30 [c]	2.0024	303
			$a(2N_{1,4})$		$a(2H_{2,3})$		$a(2H_{NH})$		
Radical Cation VA			7.35		4.85		7.54	2.0032	293
Radical Cation VB			6.57		5.69		6.94	2.0033	293

[a] $a(Sn)$ 16.48 G; $da(Sn)/dT$ −43.5 mG deg^{-1}; spectrum not completely averaged. [b] Doublets. [c] 1/2/1 triplet. [d] $a(Sn)$ 23.62 G; $da(Sn)/dT$ −34.7 mG deg^{-1}; spectrum completely averaged.

temperatures the well resolved spectrum (Fig. 1) can be satisfactorily simulated in terms of a single species with the coupling constants given in Table 1. When $HGePh_3$ is substituted for $HSiPh_3$ in the reactant mixture, the asymmetry of the spectrum is apparent over the complete temperature range and it can be simulated in terms of two overlapping species whose relative intensities vary with temperature.

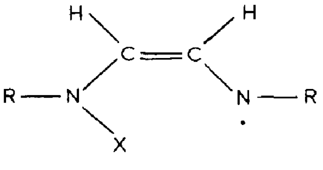
The behaviour with triphenylstannyl radicals is less straightforward. At high temperature (353 K) a single radical is observed. The spectrum consists of a quintet of triplets indicating coupling to two equivalent ^{14}N nuclei and two equivalent protons. However, the proton triplet exhibits a strong alternating linewidth effect indicative of a dynamic process (Fig. 2). At lower temperatures a different quintet of triplets is observed with no linewidth alternation. The high temperature spectrum exhibits a coupling to ^{117}Sn and ^{119}Sn with a marked negative temperature dependence.

A number of experiments have also been performed using i-Pr-DAB in place of t-Bu-DAB. The spectrum obtained with $SiPh_3H$ is complex but at least two species seem to be present. With $GePh_3H$ the spectrum can be analysed in terms of two overlapping patterns, one with rather broad lines, and the coupling constants in Table 1. The behaviour with stannyl radicals is similar to that found with t-Bu-DAB but without linewidth alternation. The tin splitting again has a negative temperature dependence.

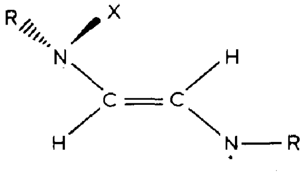
Radicals have also been observed when t-Bu-DAB is photolysed in t-butylbenzene containing di-t-butylperoxide and a trace of trifluoroacetic acid. The intense, well resolved spectrum would be analysed in terms of two species with the coupling constants in Table 1.

Discussion

Addition to t-Bu-DAB is expected to produce radicals of general formula $Bu^tN(X)\dot{C}HCH{=}NBu^t$ containing a 1-azaallylic system. The strong double-bond character of the C–C linkage should lead to a high barrier to internal rotation and



(VIA)



(VIB)

the adducts would be expected to exist in *cis* and *trans* isomeric forms VI. Our results indicate that this is generally the case.

The single species observed on addition of $\cdot SiPh_3$ to t-Bu-DAB at high temperatures exhibits, as expected, large and small couplings to ^{14}N and ^1H nuclei and in addition a splitting from a single t-butyl group (Fig. 1). One of the adducts formed by $\cdot GePh_3$ is characterised by sharp lines whereas the other has broad lines indicative of unresolved structure from a t-butyl group. One might expect the t-butyl splitting to arise from the nitrogen which has not undergone addition and is characterised by the larger spin density, but, if this were the case, a similar splitting would be expected in each isomer. We therefore suggest that the t-butyl splitting arises from the N(X)Bu^t group. We can then attempt to assign the *cis* and *trans* isomers by considering the conformational preferences of the aminyl group. In the *trans* isomer VIB the N(X)Bu^t group can adopt a position in which it is twisted perpendicular to the radical plane. The silyl or germyl group then eclipses the π-orbital containing the unpaired electron and stabilisation can arise by hyperconjugative interactions between the SOMO and the N–M bond. This structure is consistent with the conformations adopted by Group IVB groups in β-substituted ethyl radicals. Moreover, it also places the t-butyl group in favourable position for interaction with the SOMO. In the *cis* isomer VIA the twisted conformation of the aminyl group is less favourable because of repulsion between lone pairs on the two nitrogen atoms. However, if the substituent X lies in the radical plane, there is a possibility of partial coordination with the second nitrogen atom. The t-butyl group is then unable to interact with the SOMO and no coupling is expected.

We therefore suggest that the silyl adduct and the germyl adduct with broader lines in its ESR spectrum should be assigned to the *trans* conformation VIB. The other germyl adduct is the *cis*-isomer VIA. As additional support for this assignment we note that the difference between the two nitrogen coupling constants is substantially smaller for the *cis* isomer as might be expected if there is partial coordination between the germyl group and the second nitrogen.

The two radicals observed in the reaction of $\cdot GePh_3$ with i-Pr-DAB are tentatively also assigned as *cis* and *trans* adducts but the hyperfine splittings (Table 1) do not compare well with those of the t-Bu-DAB analogues. Moreover each species shows resolvable coupling to only one nitrogen atom. The presence of $HGePh_3$ is essential for radical formation: no signals were detected when di-t-butyl peroxide was photolysed in t-butylbenzene containing only i-Pr-DAB.

The reaction of t-Bu-DAB with $\cdot SnPh_3$ radicals is reminiscent of the reported behaviour of biacetyl in its reactions with stannyl [2b] and plumbyl [11] radicals. Two adducts are observed, one showing a regular binomial septet and the other a septet with a strong alternating linewidth effect. The former has been assigned to a rapidly fluxional *cis* structure and the latter to a more slowly fluxional *trans* structure. It seems likely that a similar situation applies in the case of the t-Bu-DAB adducts.

We have not been able to observe the radical exhibiting linewidth alternation over a sufficient range of temperatures to study the dynamics of the exchange process in any detail. However, we note that at 353 K, as shown in Fig. 2, the nitrogen splittings are fully averaged but the central lines of the proton triplets are severely broadened. The exchange rate is therefore comparable with the frequency difference between the two proton splittings which are expected to differ by more than the two ^{14}N splittings (cf. the silyl and germyl adducts).

If the radical exhibiting linewidth alternation is the *trans* isomer, the large ^{117}Sn and ^{119}Sn satellite splitting can be explained in terms of the conformation VIB in which the aminyl group is twisted out of the molecular plane. One would then expect a substantial positive tin coupling arising from hyperconjugation. As the temperature is raised increased torsional motion of the aminyl group will lead to a decrease in the coupling in accord with the observed negative temperature dependence.

It should be emphasized that the ratio of *cis* and *trans* isomer observed by ESR in systems of this type does not generally correspond to thermodynamic equilibrium but depends rather on a combination of kinetic and thermodynamic considerations. This has been established for both the stannyl [2b] and the monoprotonated [12] adducts of biacetyl by noting that the observed *cis* to *trans* ratio depends on the method of preparation.

The radicals formed when t-Bu-DAB was photolysed in the presence of di-t-butylperoxide and a trace of trifluoroacetic acid are believed to be the isomeric radical cations VA and VB. Photolysis of pyrazine under the same conditions leads to the formation of the known *N*,*N'*-dihydropyrazine radical cation. The larger of the triplet splittings is assigned to the N–H protons since the ^{14}N and ^{1}H coupling constants are generally very similar in magnitude for radicals of this type. The ratio of the two isomers is temperature dependent. At 293 K they appear in roughly equal amounts, but at 343 K the species with the larger ^{14}N splitting and lower *g*-value is much more abundant. We tentatively assign this to the *trans* structure since the *trans*-species appear to be favoured at high temperatures in the other systems we have investigated, but the grounds for this assignment must be considered speculative.

Experimental

N,*N'*-Di-t-butyl-1,4-diaza-1,3-butadiene was prepared from aqueous glyoxal and t-butylamine as described by Clopath and Zelewsky [6]. The di-i-propyl compound was similarly prepared from i-propylamine. The other compounds used were commercial samples. The radicals were generated by photolysis of the reactants in solution of t-butylbenzene and di-t-butylperoxide. $SiPh_3H$, $GePh_3H$, $SnPh_3H$ and $Bu_3SnSnBu_3$ were used as sources of the organometallic radicals.

A 1 kW high-pressure mercury lamp was used for photolysis. ESR spectra were recorded on a Bruker ER-200 spectrometer as previously described [3].

Acknowledgement

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