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Regioselectivity of the addition of Group IVB organometallic radicals to substituted benzo[2,1,3]thiadiazoles. An ESR investigation

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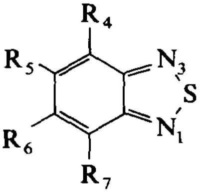
Abstract

Silyl, germyl, and stannyl radicals have been reacted with a variety of ring substituted benzo[2,1,3]thiadiazoles, and the paramagnetic adducts resulting from addition to one of the heterocyclic nitrogens have been characterized by means of ESR spectroscopy. Reactions with unsymmetrically substituted substrates lead to the formation of two distinct isomeric adducts, whose relative amounts depend on the steric and electronic effects exerted by the substituents. With compounds bearing a substituent in position 5, the amount of each individual isomeric adduct appears to be directly related to the extent of its resonance stabilization. Substituents in position 4 can be divided into two classes: those exerting only steric effects (Me, Cl) direct the addition to the less hindered nitrogen, while substituents like MeO and, to a lesser extent, CN favour radical attack on the closer, although more hindered nitrogen. Upon increase in the temperature a reversal of the relative stability of the two species is sometimes observed.

Introduction

The addition reaction of silyl, germyl, and stannyl radicals with pyridines [1–4], pyrazines [5], imines [6], and diazobutadienes [7] is known to give paramagnetic adducts resulting from the attachment of the organometallic radical to the nitrogen atom. With compounds containing two inequivalent nitrogens capable of undergoing radical attack, such as 2,6-dimethylpyrazine and 2-chloro- or 2,6-dichloropyrazine, addition of Group IVB radicals has been reported to take place specifically at the less hindered nitrogen [5], indicating that in these substrates steric repulsive effects constitute the only important factor determining the site of attack of the organometallic radical.

Since benzo[2,1,3]thiadiazoles are expected to undergo readily addition of Group IVB radicals, and since their derivatization by ring substitution is more readily achieved than for pyrazines, they provide an ideal class of compounds for studying the effect of the substituents on the selectivity of the radical attack on the two nitrogen atoms. We have therefore carried out an ESR investigation on the reaction of silyl, germyl, and stannyl radicals with benzo[2,1,3]thiadiazole (**1**) itself and its mono- and di-substituted derivatives (**2**–**11**) shown below.



(**1**: $R_4 = R_5 = R_6 = R_7 = H$; **2**: $R_4 = R_7 = Me$; **3**: $R_4 = R_7 = OMe$; **4**: $R_4 = R_5 = Me$; **5**: $R_4 = Me$, $R_5 = OMe$; **6**: $R_4 = OMe$; **7**: $R_4 = Cl$; **8**: $R_4 = CN$; **9**: $R_5 = OMe$; **10**: $R_5 = Cl$; **11**: $R_5 = CN$)

Results

The organometallic adducts were generated either by irradiating oxygen-free t-butylbenzene solutions of the benzothiadiazole and triphenylsilane, triphenylgermane, tributyltin hydride or triphenyltin hydride containing some di-t-butyl peroxide at or above room temperature, or by photolyzing at temperatures between 100 and 200 °C a melt of the substrate and the metal hydride. In the latter case the formation of the silyl, germyl, or stannyl radical can be presumably ascribed to hydrogen abstraction from the parent hydride by some excited state of the benzothiadiazole.

The spectral parameters of the resulting adduct radicals (Tables 1–4) indicate that the attack of $R_3M\cdot$ occurs at one of the nitrogen atoms of benzothiadiazole, as

Table 1

ESR spectral parameters (hfs constants in gauss $= 10^{-4}$T) for the radical adducts of **1**, **3**, **4**, and **5** with Group IVB radicals, $R_3M\cdot$

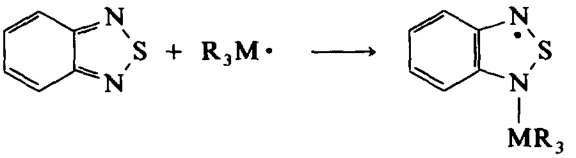
Comp.	R_3M	a_{N1}	a_{N3}	a_4	a_5	a_6	a_7	g	T (°C)
1	Ph_3Si	3.30	7.82	2.86	0.21	3.30	0.21	2.0037	25
1	Ph_3Ge	4.29	7.55	2.81	< 0.1	3.22	< 0.1	2.0035	25
1	Ph_3Sn	4.55	7.35	2.74	< 0.1	3.05	0.18	2.0034	25
3	Ph_3Si	3.60	7.85	–	0.55	2.95	–		200
3	Ph_3Ge	4.85	7.60	–	0.40	2.70	–		160
3	Bu_3Sn	5.20	7.30	–	< 0.2	2.55	–		140
4	Ph_3Si	3.55	7.60	2.05(Me)	0.27(Me)	3.35	0.36		170
4	Ph_3Ge	4.43	7.45	2.07(Me)	< 0.2	3.40	< 0.2		100
4	Bu_3Sn	4.80	7.15	2.04(Me)	< 0.2	3.21	< 0.2		50
5	Ph_3Si	3.70	7.27	2.00(Me)	–	3.35	0.25		130
5	Ph_3Ge	4.60	7.10	1.95(Me)	–	3.65	< 0.2		100
5	Bu_3Sn	4.95	6.90	1.90(Me)	–	3.50	0.15		50

Table 2

ESR spectral parameters (hfs constants in gauss = 10^{-4}T) for the radical adducts of **6**–**8** with Group IVB radicals, $R_3M\cdot$

Comp.	R_3M	Isomer	a_{N1}	a_{N3}	a_4	a_5	a_6	a_7	T (°C)
6	Ph_3Si	**C**	3.85	7.71	0.23(3H)	0.58	2.75	0.58	50
		D	7.80	3.60	–	2.60	0.25	2.30	
6	Ph_3Ge	**C**	4.38	7.79	0.21(3H)	0.40	3.22	0.40	150
		D	7.55	4.85	–	2.61	< 0.2	2.18	
6	Ph_3Sn	**C**			undetectable				70
		D	7.40	5.15	–	2.40	< 0.2	2.16	
7	Ph_3Si	**C**	3.44	7.24	–	< 0.2	3.44	< 0.2	120
		D	7.55	3.45	–	3.45	0.55	2.90	
7	Ph_3Ge	**C**	4.40	7.28	–	< 0.2	3.04	< 0.2	100
		D			undetectable				
8	Ph_3Si	**C**	3.50	6.92	0.30(1N)	0.81	2.74	0.61	50
		D	7.82	3.06	–	4.08	0.56	3.06	
8	Ph_3Ge	**C**	4.42	6.58	0.30(1N)	0.81	2.74	0.61	50
		D	7.16	3.86	–	3.94	0.43	3.86	
8	Ph_3Sn	**C**	4.60	6.28	0.32(1N)	1.30	2.52	0.98	50
		D	6.82	4.04	–	4.04	0.34	4.04	

depicted in Eq. 1.



(1)

The assignment of the proton hyperfine splitting constants was made on the basis of the mesomeric system for the radical adducts and by comparison with those of

Table 3

ESR spectral parameters (hfs constants in gauss = 10^{-4}T) for the radical adducts of **9**–**11** with Group IVB radicals, $R_3M\cdot$

Comp.	R_3M	Isomer	a_{N1}	a_{N3}	a_4	a_5	a_6	a_7	T (°C)	E/F
9	Ph_3Si	**E**	3.70	7.30	2.20	–	3.70	< 0.2	120	–
		F			not interpreted					
9	Ph_3Ge	**E**	4.80	7.07	2.15	–	3.80	< 0.2	80	0.8
		F	8.01	4.00	0.32	0.32(3H)	0.32	2.95	80	
10	Ph_3Si	**E**	3.44	7.50	2.80	–	3.42	< 0.2	90	ca. 1
		F	7.60	3.20	0.25	0.2(1Cl)	0.40	3.30		
10	Ph_3Ge	**E**	4.47	7.16	2.71	–	3.24	0.23	90	ca. 0.9
		F	7.45	4.15	0.15	0.2(1Cl)	0.10	3.12		
11	Ph_3Si	**E**	3.27	7.51	2.65	–	3.20	0.13	90	0.3
		F	6.59	3.55	0.75	0.55(1N)	0.37	2.99		
11	Ph_3Ge	**E**	3.91	7.56	2.64	–	3.25	0.44	90	0.5
		F	6.69	4.52	0.59	0.59(1N)	< 0.2	2.93		

Table 4

Relative amounts of the isomeric adducts of Group IVB radicals $R_3M\cdot$ with compounds **6–8**

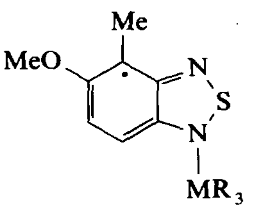
Comp.	R_3M	T (°C)	C (%)	D (%)	T (°C)	C (%)	D (%)
6	Ph_3Si	50	50	50	280	> 95	< 5
6	Ph_3Ge	25	< 10	> 90	150	45	55
6	Ph_3Sn	70	< 5	> 95			
7	Ph_3Si	120	90	10			
7	Ph_3Ge	100	> 95	< 5			
8	Ph_3Si	25	33	66	200	83	17
8	Ph_3Ge	50	45	55	140	95	5
8	Ph_3Sn	50	64	36			

the substituted derivatives. The smaller of the two nitrogen splittings was assigned to the atom undergoing radical attack, since both its magnitude and its variation with the nature of the entering organometallic group are similar to those found for the related adducts of pyridines [4].

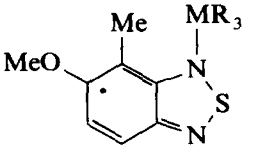
When the UV irradiation is interrupted at room temperature the signal of the silyl and germyl adducts from **1** decays to an equilibrium value in a process showing reasonably clean second order kinetics, the radical half-life being of the order of tens of seconds. This indicates that dimerization is the more important termination process for these radicals. The occurrence of dimerization is further supported by the fact that the intensity of the ESR spectra can be increased or decreased reversibly by raising or lowering the temperature in the absence of UV light.

*4,7-Disubstituted benzothiadiazoles (**2**,**3**).* In compounds **2** and **3** the nitrogens are equivalent, as in benzo[2,1,3]thiadiazole (**1**), but the presence of the methyl or methoxy substituents in the proximity of the sites of attack might render the addition by the organometallic radical more difficult than in **1** if only steric effects were operative. In fact, attempts to generate the adducts from the dimethyl derivative **2** were unsuccessful with either silyl or germyl or stannyl radicals even at temperatures as high as 200 °C. In contrast, irradiation of the melts of the dimethoxyderivative **3** and the organometallic hydrides at $T > 100$ °C inside the cavity of the EPR spectrometer led to intense signals due to the expected adducts (see Table 1). It therefore appears that with methoxy substituents the steric repulsion to the approach of the Group IVB radical to the nitrogen atoms is overcome by some other effect that assists the radical addition.

*4,5-Disubstituted benzothiadiazoles (**4**,**5**).* Radical adducts are readily formed from both of the asymmetric derivatives **4** and **5**. In principle two isomeric radicals could be obtained depending on which of the two inequivalent nitrogens is attacked. The ESR spectra clearly show that only one radical adduct is formed from either substrates, namely the one resulting from attack at the less hindered nitrogen. The identity of the observed species could be inferred from the value of the methyl proton splitting in the radical from **5**, which is expected to be ca. 2–3 G, as in fact observed, if addition takes place at N-1 (see structure **A**) and less than 0.5 G if the addition occurs at N-3 (see structure **B**). This assignment is also consistent with the fact that compound **2**, bearing methyl groups at both positions 4 and 7, did not give any adduct.

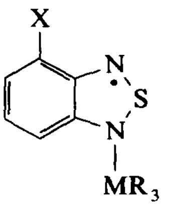


(A)

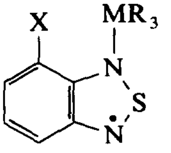


(B)

4-Substituted benzothiadiazoles (6–8). In contrast with the previous two cases, when $Ph_3Si\cdot$ radicals reacted with 4-methoxybenzo[2,1,3]thiadiazole (**6**) the superimposition of the two spectra due to the isomeric adducts **C** and **D** (X = OMe) was observed. The structural assignment was made on the basis of the magnitude of the ring proton splittings, the species showing one large (ca. 3 G) and two small (< 1 G) couplings being identified as **C**, and the other, showing two large and one small proton splitting, as **D**. Computer simulation of the experimental spectra allowed the determination of the relative amount of the two species to be made. The isomer ratio proved to be strongly temperature dependent: at near room temperature **C** and **D** are present in roughly equal amounts, but when the temperature is raised, adduct **C** becomes predominant, and is practically the only detectable species at 280 °C. It should be pointed out that the isomer ratios given in Table 4 are only indicative, since they were derived from computer simulation of the ESR spectra, and therefore are very sensitive to the linewidth values chosen for the two species, and since the actual amount of the two radicals was slightly dependent on the history of the sample (see Discussion).



(C)



(D)

The room temperature ESR spectra of the germyl adduct of **6** is essentially due to isomer **D** (see Fig. 1), but as the temperature is raised new lines, due to isomer **C**, grow in the spectra, and at ca. 150 °C the two isomeric adducts are present in nearly equal amounts.

Finally, reaction of stannyl radicals with **6** at slightly above room temperature gives **D** as the only observable radical. At higher temperature the ESR spectra are too weak to be interpreted.

The reaction of triphenylsilyl radicals with 4-chlorobenzo[2,1,3]thiadiazole (**7**) at 120 °C also afforded the two isomeric adducts **C** and **D** (X = Cl) in an approximate ratio of 9 : 1, respectively, the temperature in this case having little influence on the relative concentration of the two species. Only isomer **C** could be observed in the

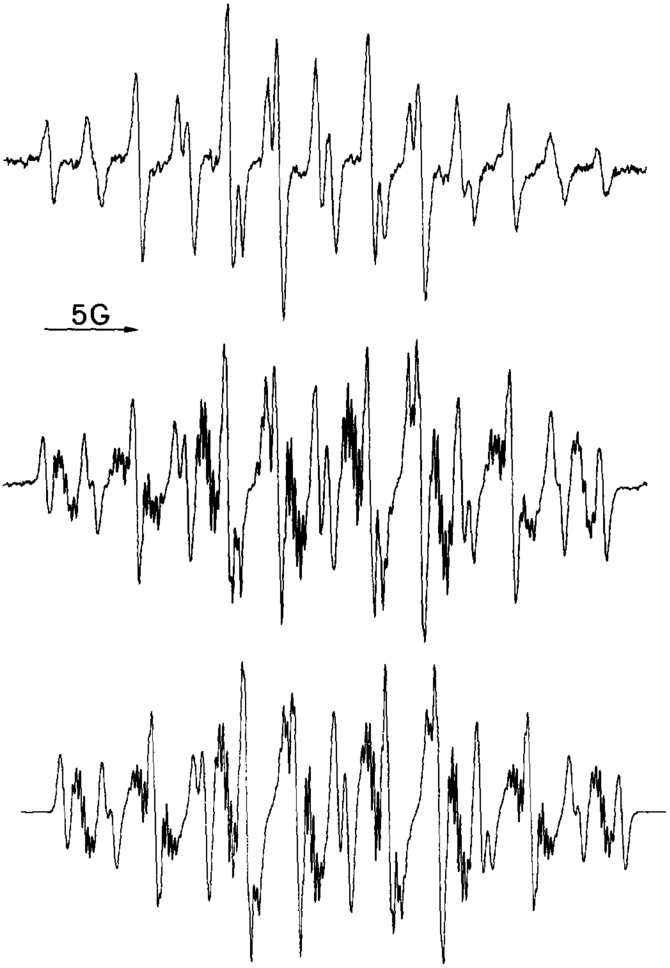
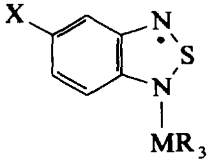


Fig. 1. ESR spectra observed in the reaction of 4-methoxy-benzo[2,1,3]thiadiazole with triphenylgermyl radicals at room temperature (top) and at 150 °C (centre), with a computer simulation (bottom).

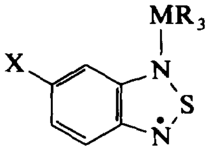
reaction of triphenylgermyl radicals with **7**, and no ESR signal could be detected in the reaction with stannyl radicals.

Like the 4-methoxy derivative, the reaction of Group IVb radicals with 4-cyanobenzo[2,1,3]thiadiazole (**8**) led to the formation of both the isomeric adducts **C** and **D** (X = CN), their relative amounts being strongly dependent on temperature. Thus the two species were present in comparable amounts near to room temperature, whilst isomer **C**, resulting from attack on the less hindered nitrogen, predominates at higher temperature (see Tables 2 and 4).

5-Substituted benzothiadiazole (9–11). When the 5-substituted derivatives **9–11** reacted with silyl or germyl radicals, ESR spectra showing the presence of the two isomeric species **E** and **F** were obtained (see Table 3). With stannyl radicals the ESR signals were too weak in the case of compounds **9** ($X = OCH_3$) and **10** ($X = Cl$), and too complex in the case of **11** ($X = CN$), to be interpreted.



(E)



(F)

The relative ratio of the two isomeric adducts was not sensitive to temperature variations over a wide range. Isomer **F** was predominant in the adducts of the 5-cyano derivative (**11**), and present in an amount comparable with that of **E** in the adducts of 5-methoxy (**9**) and 5-chloro (**10**) benzothiadiazoles.

Discussion

The investigated benzothiadiazoles may be divided in two classes: one comprising compounds **2**–**8** bearing substituent(s) in position 4 and/or 7, where they can affect the addition reaction of the organometallic radical to the nitrogen atoms both by steric hindrance and by electronic effects, and another comprising compounds **9**–**11** where the substituent is in position 5 and so too far away from the possible reaction centers to influence the addition by steric effects.

In the latter class the amount of the individual isomeric adducts is related to the degree of resonance stabilization exerted by the substituent. This is predicted to be large for substituents occupying a position of high spin density, as in the adducts **F**, and small for substituents attached to carbon atoms of low spin density, as in adducts **E**. Moreover this stabilizing effect should be greater for cyano than for methoxy or chlorine substituents, since the CN group can more readily delocalize the unpaired electron. In fact isomer **F** is about three times more abundant than isomer **E** in the adducts of **11** ($X = CN$), but only slightly in excess in adducts from **9** ($X = OCH_3$) and **10** ($X = Cl$). The absence of marked temperature effect on the isomer ratio is entirely expected on the basis of the above interpretation.

The experimental results for the first class of benzothiadiazoles are more intriguing. In compounds containing a substituent in position 4 the addition to the nitrogen in position 3 should be largely disfavored both because of the steric repulsion by the substituent to the approach of the entering radical, and because of the absence of resonance stabilization in the resulting adduct in which the unpaired electron cannot be delocalized over the substituent. Indeed this is the case with methyl- (**4** and **5**) and chlorine-substituted compounds **7** in which the less hindered adduct is essentially the only observable species. In this respect the failure to detect any ESR signal at all when reacting $\cdot MR_3$ radicals with 4,7-dimethylbenzo[2,1,3]-thiadiazole (**2**) is not surprising.

On the other hand, with 4-methoxy and 4-cyano substituents, the addition of Group IVB radicals at near room temperature takes place preferentially at the more hindered nitrogen, i.e. that in position 3. This means that the steric repulsion to the approach of the $R_3M\cdot$ radical is largely overcome by some other effect which assists the radical addition. Since Group IVB atoms, especially germanium and tin can be readily coordinated by electron rich elements such as oxygen or nitrogen, we suggest that partial complexation of the entering radical by the methoxy or cyano group in the proximity of the nitrogen in position 3 assists the attack on this atom.

When the temperature is raised, significant changes in the ratios between isomers **C** and **D** are observed in the silyl and germyl adducts of compounds **6** and **8**, the more abundant species becoming **C**, the one resulting from addition at nitrogen in position 1 (see Table 4). This behaviour can be rationalized in terms of the different persistence of the two isomeric adducts. Signal decay curves and temperature jump experiments have clearly demonstrated that these adducts are in equilibrium with their dimers. It is conceivable that dimerization occurs at the positions of higher spin density, i.e. the nitrogen which has not undergone radical attack. On this basis one should expect isomer **C** to dimerize less readily than **D** because of the presence of the substituent in the neighbourhood of the nitrogen involved in the radical combination process. Moreover the monomer–dimer equilibrium is expected to be more shifted toward the monomer for adducts **C** than for adducts **D**, especially at high temperature. We therefore suggest that at ordinary temperatures the isomer ratio reflects the relative rate constants for addition of $R_3M\cdot$ radical on either of the two nitrogen atoms, and at higher temperatures is determined by the relative ease of dimerization of the two species. This explanation is consistent with the fact that the ratio *C/D* depends significantly not only on the temperature but also on the history of the sample. Samples irradiated for longer periods, in which a considerable amount of dimer has built up, show higher **C/D** ratios than freshly prepared samples.

Conclusions

Benzo[2,1,3]thiadiazoles have been found to undergo ready radical addition of silyl, germyl and, to a minor extent, stannyl radicals to give markedly persistent cyclic thioaminyl radicals, which were detected by ESR spectroscopy. The presence of a substituent in positions 4 or 5 leads to isomeric adducts, which can be identified from their spectral parameters. The relative stability of the two possible isomers from 5-substituted substrates is essentially dictated by the possibility of delocalization of the unpaired electron into the substituent itself. For 4-substituted substrates two classes of substituents can be envisaged: those exerting mainly steric effects, such as methyl or chlorine, undergo direct addition to the less hindered nitrogen in position 1, while electron rich substituents, such as the methoxy and cyano groups, facilitate presumably by partial coordination of the Group IVB element, addition to the nitrogen in position 3, despite the fact that this is the more hindered site for attack.

In all cases the radicals are in equilibrium with their dimers; as a consequence, the isomer ratio in the adducts from 4-substituted compounds varies considerably with the experimental conditions. Thus radical adducts whose formation is kinetically disfavoured at room temperature, become the more abundant species at high temperature owing to a shift of the monomer–dimer equilibrium toward the monomers involving the greater steric hindrance to dimerization.

Experimental

Benzo[2,1,3]thiadiazole (**1**) and all the organometallic compounds were commercial products, while 4,5-dimethyl- (**2**) [8], 4,7-dimethoxy- (**3**) [9], 4,7-dimethyl- (**4**) [8], 4-methyl,5-methoxy- (**5**) [8], 4-methoxy- (**6**) [8], 4-chloro- (**7**) [10], 4-cyano- (**8**) [11], 5-methoxy- (**9**) [8], 5-chloro- (**10**) [10], and 5-cyano-benzo[2,1,3]thiadiazole (**11**) [11] were prepared by previously described procedures.

In a typical ESR experiment, a sample, consisting either of a nitrogen purged t-butylbenzene solution of the appropriate thiadiazole (ca. 10^{-2} *M*), the organometallic hydride (ca. 10^{-2} *M*), and di-t-butyl peroxide (ca. 0.5 *M*), or of a melt (1 : 5 w : w) of the thiadiazole in the neat organometallic compound, was irradiated inside the cavity of an ESR spectrometer with light from a high pressure mercury lamp (Hanovia, 1 kW). The spectra were recorded by means of a spectrometer (Bruker ER 200D or ESP 300) equipped with standard variable temperature accessories, an NMR gaussmeter for the calibration of the magnetic field, and a frequency counter for the determination of *g*-factors, which were calibrated by reference to the value for the perylene radical cation ($g = 2.0025_8$).

When two radical species were simultaneously observed, their relative amounts were estimated by double integration of the signals and by careful computer simulation of the experimental spectra.

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