RECENT DEVELOPMENTS IN THE FIELD OF ORGANIC DERIVATIVES OF GROUP IV B ELEMENTS

WILHELM P. NEUMANN

Universität Dortmund, D4600 Dortmund-Hombruch, August-Schmidt-Straße 6

ABSTRACT

Formation of perarylated cyclosilanes and cyclogermanes from diaryl dihalides and lithium, sodium or sodium–naphthalene is assumed to proceed by a step-wise catenation of the Wurtz type. Degradation in the mass spectrometer takes place mainly by elimination of respectively carbene-like Ar_2Si or Ar_2Ge moieties.

Formation of free radicals from organotin compounds by radical breakdown of different bonds around the tin atom is investigated. A table with present 'best values' for D_{Sn-X} is given. They vary in the range between ~ 35 (Sn–H) and 95 (Sn–OCOR) kcal/mole. Organotin hydrides are very strong radical scavengers.

In the chemistry of stannyl radicals $R_3Sn\cdot$, various substitutions of the type S_R2 have been found. With diacyl peroxides and peresters, the peroxide bridge is attacked. Attention has been given to the different transition states. As shown by the influence of π-electron density, $R_3Sn\cdot$ is strongly nucleophilic. Some azo compounds $R-N{=}N-X-R'$ (X = O, S, SO_2, NR''), hydrazines and pentaz-dienes are degraded rapidly and by a similar mechanism.
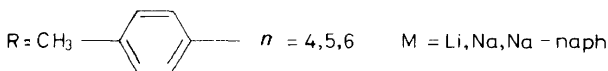

A. INTRODUCTION

IN THE last 15 years, an increasing number of observations have led to the conclusion that some covalent bonds around the elements of group IV B have a surprisingly high reactivity. New chemistry of organic derivatives of this group has been developed. The bonds (M = Si, Ge, Sn, Pb) M—H, M—N and M—O merit special attention here, but a number of M—C and M–metal bonds are also of new importance. This has led not only to con-siderable progress in preparative chemistry, but also to a better understanding of reaction mechanisms. In this connection, it should not be forgotten that carbon is the first element of group IV B, and that conclusions from theoretical organic chemistry have stimulated some of the investigations in the field to be considered here.

Some recent developments made by the author's group will be reported, coming from the Institute of Organic Chemistry of the University of Giessen up to spring 1969, and currently from the Laboratories of Organic Chemistry of the new University of Dortmund.

B. NEW EVENTS IN THE CHEMISTRY OF CYCLOSILANES AND CYCLOGERMANES

Perphenylated cyclo-silanes and -germanes with 4-, 5- or 6-membered rings became known in recent years through the work of Professor Henry Gilman and his co-workers[1] as well as that of my student K. Kühlein and myself[2,3]. We sought to bring more insight into some details of formation and of behaviour of these peculiar compounds. For these studies, my student Michael Richter[4] took the p-tolyl residue bound to Si or Ge. Using the classical method, he prepared the 4-, 5- and 6-membered rings, starting from either p-Tol$_2$SiCl$_2$ or p-Tol$_2$GeCl$_2$. (The latter was prepared in satisfying purity from the dihydride with carbon tetrachloride.) (See *Scheme 1*.)

$$nR_2SiCl_2 \quad + \quad 2nM \longrightarrow (R_2Si)_n \quad + \quad 2n\,MCl$$

$$nR_2GeCl_2 \quad + \quad 2nM \longrightarrow (R_2Ge)_n \quad + \quad 2n\,MCl$$

R = CH$_3$ —⟨benzene ring⟩— n = 4,5,6   M = Li, Na, Na – naph

				Polymers
m.pt (decomp.)	237°–246°	292°–307°	>360°	oil
sol. in cold benzene	sparingly	well	not	well

*Scheme 1* (after Richter and Neumann, 1969)

It is surprising that the melting points and solubilities shown in *Scheme 1* are quite similar or even identical for the corresponding silyl and germyl rings. The same can be seen by comparing corresponding p-tolyl and phenyl derivatives[1,2].

Scheme 2 is concerned with the mechanism of ring formation. It could be thought—and Russian workers drew attention to this in the case of similar tin compounds[5]—that carbene-like silylenes or germylenes work as intermediates here.

They may arise from compounds, e.g. R$_2$Ge(Cl)M by α-elimination, a type of reaction well known in the chemistry of carbenes. If this takes place, a germylene should appear (and its polymers too) by reacting R$_2$GeCl$_2$ with R′Li, see *Scheme 2*. However, we failed to detect any trace of polymeric (R$_2$Ge)$_n$ or other following products, but found a nearly quantitative yield of R$_2$Ge(R′)Cl.

For the mechanism, we prefer a stepwise prolongation of the chain by reactions of the Wurtz type. Polymers can be formed; but, if there is a proper steric conformation, ring closure occurs. With our bulky p-tolyl
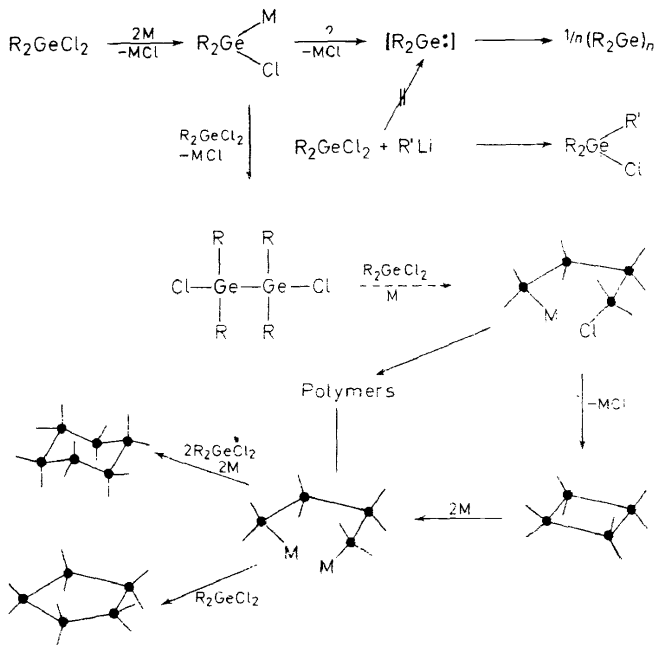
Scheme 2

residues, the horse-shoe conformation (*Scheme 2*) is a preferred one, and the 4-membered ring is formed first. If one provides a lack of reactive metal atoms—easy to establish when using sodium turnings or lithium wire— this product can be isolated in yields up to 60 per cent. Moreover, it is split off quickly by excess of alkali metal atoms, forming both polymers and a mixture of 5- and 6-membered rings. The 4-membered ring disappears from the reaction mixture. When we used a very finely divided suspension of sodium (5 microns) or, even more effective, a sodium–naphthalene solution, we could not detect any Ge_4-ring, but found only the 5- and 6-membered ones.

Up to now, there is no proof of the occurrence of carbene-like silylenes and germylenes as intermediates in solution. But in a high vacuum and caused by electron impact, they do occur. Using a Varian CH 5 mass spectro-meter and its normal inlet equipment, we found the following series of degradation products[4, 6], see *Scheme 3*. (The germanium derivatives are shown as an example here.) The molecular peaks can be seen, in the case of Ge_5 and Ge_4, with striking intensity. This means that the cyclic molecules are of considerable stability.

All cations found in the 6-membered Ge-ring are compiled in *Scheme 4* to propose a main degradation pathway. Carbene-like Tol_2Ge is the main leaving group. In addition splitting of tolyl residues occurs, as well as splitting of Tol_3Ge and of $TolGe$ residues[6a]. The latter indicates a type of splitting with migration of aryl groups:

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Scheme 3. Mass spectra of Tol_8Ge_4 $Tol_{10}Ge_5$ and $Tol_{12}Ge_6$

m/e calc.	Cation	Tol_8Ge_4	$Tol_{10}Ge_5$	$Tol_{12}Ge_6$	m/e calc.	Cation	Tol_8Ge_4	$Tol_{10}Ge_5$	$Tol_{12}Ge_6$
1529	$Tol_{12}Ge_6$			1	947	Tol_8Ge_3			6
1438	$Tol_{11}Ge_6$			6	856	Tol_7Ge_3			17
1347	$Tol_{10}Ge_6$			16	765	Tol_6Ge_3	20	3	28
1256	Tol_9Ge_6			9	673	Tol_5Ge_3	20	6	20
1165	Tol_8Ge_6			2	582	Tol_4Ge_3	31	17	37
1274	$Tol_{10}Ge_5$		77	1	491	Tol_3Ge_3	4	21	30
1183	Tol_9Ge_5		4	7	400	Tol_2Ge_3	3	19	19
1092	Tol_8Ge_5		2	51	692	Tol_6Ge_2			13
1001	Tol_7Ge_5			32	601	Tol_5Ge_2	50	15	80
910	Tol_6Ge_5			6	510	Tol_4Ge_2	11	8	70
1202	$Tol_{10}Ge_4$		1	6	419	Tol_3Ge_2	27	31	60
1111	Tol_9Ge_4		4	4	327	Tol_2Ge_2	41	20	39
1019	Tol_8Ge_4	100	5	5	236	$TolGe_2$	8	7	46
928	Tol_7Ge_4	4	100	11	437	Tol_4Ge			35
840	Tol_6Ge_4	27	3	51	346	Tol_3Ge	100	100	100
746	Tol_5Ge_4			40	255	Tol_2Ge	41	46	91
655	Tol_4Ge_4			21	164	$TolGe$	100	100	100
564	Tol_3Ge_4		3	5	182	Tol_2	90	91	87

$$\begin{array}{ccc} \text{Tol} & \text{Tol} & \text{Tol} \\ | & | & | \\ -\text{Ge}-\text{Ge}- & \rightarrow & -\overset{\cdot}{\text{Ge}}\cdot + \text{Tol}-\text{Ge}- \\ | & | & | \quad\quad | \\ \text{Tol} & \text{Tol} & \text{Tol} \quad \text{Tol} \end{array}$$

$$Tol_{10}Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_8Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol_6Ge_2^{\oplus} \xrightarrow{-Tol_2Ge} Tol_4Ge^{\oplus}$$

$$\left[Tol_{11}Ge_5^{\oplus}\right] \xrightarrow{-Tol_2Ge} Tol_9Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_7Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol_5Ge_2^{\oplus} \xrightarrow{-Tol_2Ge} Tol_3Ge^{\oplus}$$

$$Tol_{12}Ge_6 \xrightarrow{-e^{\ominus}} Tol_{12}Ge_6^{\oplus} \xrightarrow{-Tol_2Ge} Tol_{10}Ge_5^{\oplus} \xrightarrow{-Tol_2Ge} Tol_8Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_6Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol_4Ge_2^{\oplus} \xrightarrow{-Tol_2Ge} Tol_2Ge^{\oplus}$$

$$Tol_{11}Ge_6^{\oplus} \xrightarrow{-Tol_2Ge} Tol_9Ge_5^{\oplus} \xrightarrow{-Tol_2Ge} Tol_7Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_5Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol_3Ge_2^{\oplus} \xrightarrow{-Tol_2Ge} Tol\,Ge^{\oplus}$$

$$Tol_{10}Ge_6^{\oplus} \xrightarrow{-Tol_2Ge} Tol_8Ge_5^{\oplus} \xrightarrow{-Tol_2Ge} Tol_6Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_4Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol_2Ge_2^{\oplus}$$

$$Tol_9Ge_6^{\oplus} \xrightarrow{-Tol_2Ge} Tol_7Ge_5^{\oplus} \xrightarrow{-Tol_2Ge} Tol_5Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_3Ge_3^{\oplus} \xrightarrow{-Tol_2Ge} Tol\,Ge_2^{\oplus}$$

$$Tol_8Ge_6^{\oplus} \xrightarrow{-Tol_2Ge} Tol_6Ge_5^{\oplus} \xrightarrow{-Tol_2Ge} Tol_4Ge_4^{\oplus} \xrightarrow{-Tol_2Ge} Tol_2Ge_3^{\oplus}$$

$$Tol_3Ge_4^{\oplus}$$

⌣ Splitting with Migration of Tolyl Residues

Scheme 4. Degradation of cyclo-$Tol_{12}Ge_6$ in the mass spectrometer

Some cations with very low tolyl contents are also worth mentioning. It seems that splitting of electrons by electron impact concerns not only Ge—Ge bonds (45 kcal)[7] and Ge—C bonds, but also electrons from the aromatic systems of tolyl residues (203 kcal)[8] and those from lower orbitals of Ge atoms (191–213 kcal)[9] (See, e.g., $Tol_6\,Ge_2^{\oplus}$ and $Tol_4\,Ge^{\oplus}$).

C. FORMATION OF FREE RADICALS FROM ORGANOTIN COMPOUNDS

The chemistry of free radicals has made considerable progress in organic chemistry during the last few years. It is not surprising, therefore, that

organometallic chemistry, which was thought for a long time to be nearly exclusively a chemistry of ions, has been reinspected recently for the occurrence of radicals.

My group was interested especially in studying organotin radicals[12]. Some observations concerning silyl and germyl radicals will be reported in a short communication during this meeting.

Around the tin atom several bonds are susceptible for radical breakdown. It would be desirable to have exact values for bond dissociation energies. One way of determining these values may be the measurement of appearance potentials for corresponding ions in the mass spectrometer and then, using a set of thermochemical data, calculation of the desired dissociation energy. Measuring of appearance potentials of rather heavy ions, like those with tin atoms, is not easy and possibly not free from errors, but should eventually be effected with satisfying results. But, unfortunately, different sets of thermochemical data are needed for the final calculations. The discussion about which ones are correct is as yet unsettled, to the author's knowledge. The first published dissociation energies[10] calculated from appearance potentials, therefore, are rather high and, at least in my experience, not in good agreement with chemical evidence. In the author's group an internal table of dissociation energies is used, *Scheme 5*. It is based on published thermochemical values, recalculation of several other data[10], and chemical experience[11].

Scheme 5. Dissociation energies D (kcal/mole) for compounds $(CH_3)_3Sn$—X

X	D (kcal/mole)	X	D (kcal/mole)
CH_3	55	NR_2	(65 to 70)
C_2H_5	50	O—COR′	~95
$CH=CH_2$	60	Cl	85
CH_2—$CH=CH_2$	~37	Br	76
CH_2—C_6H_5	39	I	62
C_6H_5	63		
$Sn(CH_3)_3$	57		
H	~35		

Of course, some of these values are empirical or at least semi-empirical. Good support is given by recent measurements[9, 10a], which give, for example, for $(CH_3)_3Sn$—CH_3 61 ± 5 or 60.5 ± 2 kcal, which is in rather good agreement with the old thermochemical value of 55 ± 5 kcal, see *Scheme 5*.

D. NEW EVENTS IN THE CHEMISTRY OF STANNYL RADICALS

Stannyl radicals $R_3Sn\cdot$ (R mostly Bu, Et or Me) have proved themselves to be useful reagents for studying radical reaction mechanisms. The author's group has an intense interest in this field of research[12–14]. Some examples of new developments will be given here.

Benzoyl peroxide is degraded by organotin hydrides very quickly by the way of a radical chain mechanism. Compared with this, the very efficient known inducing compounds like dibutyl ether are rather ineffective, see *Scheme 6*.

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Scheme 6. Half-life time of benzoyl peroxide, 0·2 M in benzene

Inducing compound 0·4 M	Temperature, °C	$t_{\frac{1}{2}}$, min
Without	80	240
C_4H_9—O—C_4H_9	75	345
C_4H_9—O—C_4H_9	60	~1800
$(C_2H_5)_3SnH$	60	14
$(C_2H_5)_3SnH$	50	53

Stannyl radicals are the attacking species. *Scheme* 7 shows what is going on with acetyl benzoyl peroxide, which has been selected for detailed studies[14].
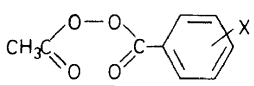

X = OC_2H_5; OCH_3; H; Cl; CN
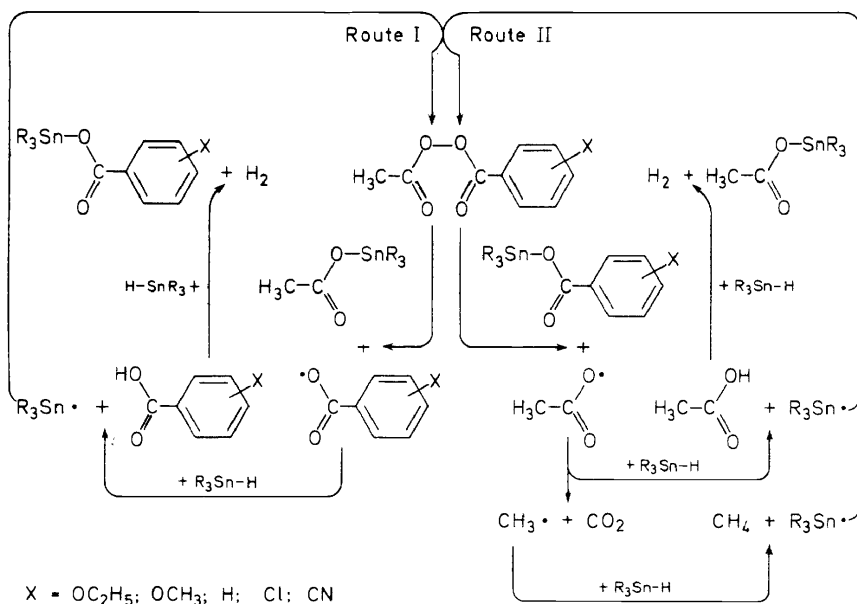
Scheme 7

The peroxide bridge is attacked by a stannyl radical, but the two oxygen atoms are not equivalent, depending upon the nature of the substituent X. The more electron withdrawing is X, the more is Route II preferred by the stannyl radical, releasing an acetoxy radical, a part of which forms CO_2 + CH_4, see *Schemes* 7 and 8.
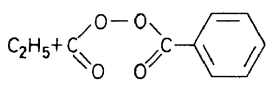
Consideration of all the available facts leads to the ratio of Route I : Route II as set out in *Scheme* 9.

A free radical always looks for places susceptible to radical attack (i.e. with high F-values, which may be given by HMO calculations). From the foregoing, however, it must be concluded that the stannyl radical is strongly

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Scheme 8. Unsym. diacylperoxide, 0·23 mol. in benzene
+ 2 mole $(C_2H_5)_3SnH$, 60·0°, Yield of products

	Mole/Mole Peroxide (±0·03)				
	CO_2	CH_4	H_2	Acetate	Benzoate
$X = p$ -C_2H_5-O -	0·23	0·22	0·64	0·76	0·95
p -CH_3 -O -	0·25	0·24	0·59	0·74	0·95
H -	0·37	0·29	0·54	0·71	0·96
p - Cl -	0·38	0·34	0·53	0·66	0·98
m - Cl -	0·50	0·45	0·40	0·52	0·95
p -NC-	0·54	0·54	0·35	0·42	0·95

	C_2H_6		Propionate	
	0·43	0·41	0·49	0·63	0·88

Route II

I   II
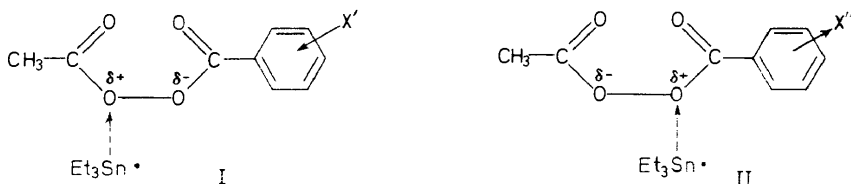
Peroxide X', X''	I	II
CH_3CO—OO—CO—C_6H_4—OC_2H_5 (p)	70%	30%
CH_3CO—OO—CO—C_6H_4—H	63%	37%
CH_3CO—OO—CO—C_6H_4—Cl (p)	56%	44%
CH_3CO—OO—CO—C_6H_4—CN (p)	36%	64%

Scheme 9 (after Rübsamen, Neumann, Ra. Sommer, Frommer. *Chem. Ber.* **102**, 1290 (1969)).

nucleophilic, always seeking the most electron-deficient place in those parts of a peroxide molecule susceptible to radical attack.
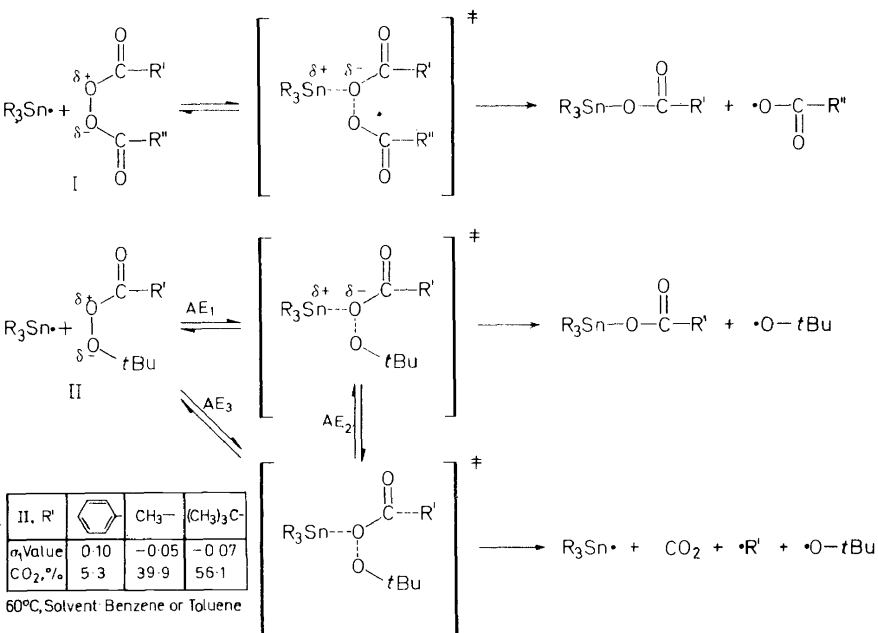
This is of interest, because most free radicals so far studied intensively are only slightly nucleophilic or even, generally, electrophilic.

Now, the transition state of the radical attack mentioned above should be considered, see *Scheme 10*. With a diacyl peroxide, only one set of products can be formed, as is known from many experiments made so far. It may be concluded, therefore, that there is only one way leading to them and only one transition state.

A different behaviour has been found with tert-butyl peresters[15]. On the one hand, the expected way with formation of stannyl ester and tert-butoxy radical (which undergoes further reactions) has been established. On the other hand induced fragmentation has been observed with evolution of

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The following table appears within Scheme 10:

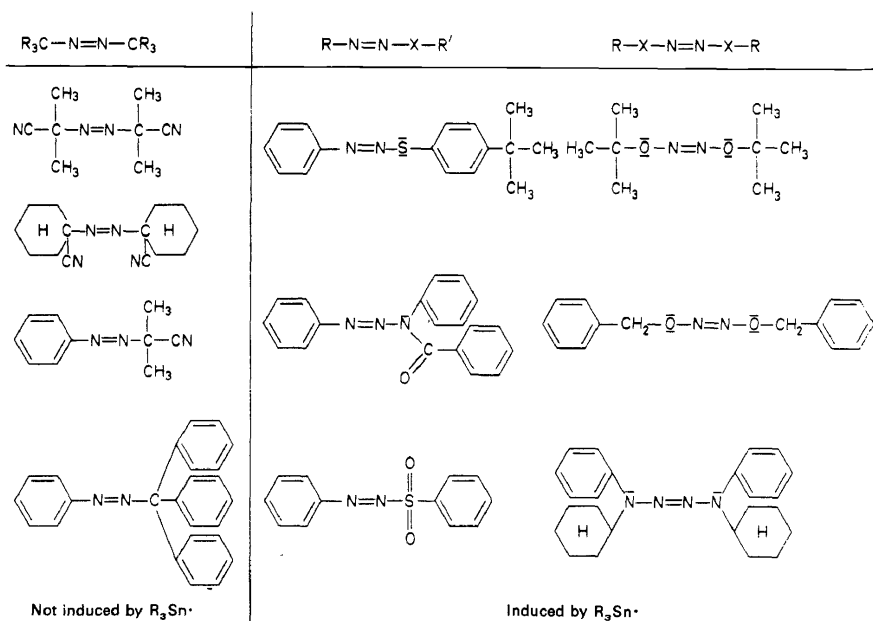| II, R'	$\langle\bigcirc\rangle$	CH_3-	$(CH_3)_3C-$
σ Value	0·10	−0·05	−0·07
CO_2,%	5·3	39·9	56·1

60°C, Solvent: Benzene or Toluene

Scheme 10

carbon dioxide and typical products (the radicals undergo further reactions), as shown in *Scheme 10*. Again, stannyl radicals are the inducing agent, ending without being bound to any of the resulting products. They finally recombine to the distannane. This is a new type of reaction, apparently not yet studied. Stannyl radicals clearly work as catalysts here. The inducing power of stannyl radicals is illustrated by the half-life time of the peresters, which is decreased by a factor of about 10^{-3}, compared with that of the corresponding spontaneous radical degradation. Therefore, two transition states can be assumed, as shown in *Scheme 10*. The lower one needs additional activation energy, $AE_3 > AE_1$, and apparently is less polar. This can be concluded from the facts that at higher temperatures (60°C) or in non-polar solvents much more carbon dioxide is evolved than at lower temperatures or in polar solvents (isobutyronitrile). R' in the perester II yields an additional influence by means of inductive effects: the higher the polarity of II, the more the 'normal way' is preferred. It should be mentioned that hitherto fragmentation was known for the pivalyl perester—but only at much higher temperatures—whereas it was uncertain for the acetic and was entirely unknown for the benzoic acid perester[16].
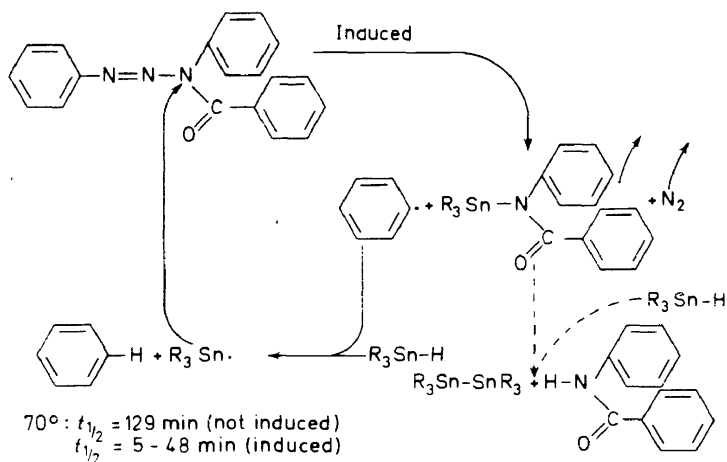
An old question for chemists concerned with radical degradation of *azo compounds* is, whether this degradation can be only of first order, or whether it may be induced by any other compound. Until 1967, the answer was: no induction is possible. But then, new aspects could be revealed by means of stannyl radicals[13]. *Scheme 11* shows some azo compounds of the types R—N=N—X—R' and R—X—N=N—X—R, which are degraded

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quickly by stannyl radicals, with evolution of nitrogen. Some recent results in this field have been published by the author's group[13].

Now, some further examples[17] should be noticed: 1,3-diphenyl-3-benzoyl-triazene, *Scheme 12*, and 1,4-diphenyl-1,4-dicyclohexyl-tetrazene, *Scheme 13*.
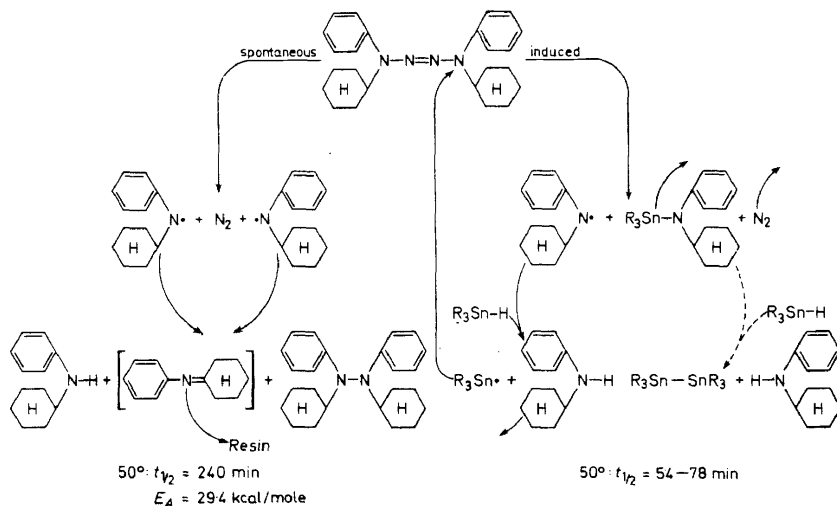

Scheme 11

$70°: t_{1/2} = 129$ min (not induced)
$t_{1/2} = 5 - 48$ min (induced)

Scheme 12

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50°: $t_{1/2}$ = 240 min
E_A = 29·4 kcal/mole

50°: $t_{1/2}$ = 54−78 min

Scheme 13

All these induced degradations are radical reactions of the type S_R2.

From investigation of a series of tetrazenes some facts governing the behaviour of the stannyl radical can be derived, see *Scheme 14*. As might be

Tetrazene – 2	$\Delta H^{\neq}$spontaneous kcal/mole,50 °C	Electron density at N_1 and N_4	Degraded by $R_3Sn\cdot$
	36	1·89	no
	28·7	1·81	quick
	28·9	1·74	very quick
	~39	≦1·74	only with AIBN

Scheme 14

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expected, the activation enthalpy is important. The higher it is, the more unlikely it is for the attacking stannyl radical to be able to afford it. But another factor can be derived, too. The more electron density is withdrawn from N_1 and N_4, the easier these spots are attacked by the nucleophilic stannyl radical. This can best be seen by comparing the second with the third tetrazene[18] in *Scheme 14*[18].

Recently, reactions of stannyl radicals with further groups of organic compounds have been found. Two examples should be included here.

Tetraphenylhydrazine dissociates, as is well known, into two diphenyl-amine radicals. If one adds a radical scavenger (as was done by Hungarian workers[19]) the half-life time could be determined, see *Scheme 15*. But, organotin hydride works not only as radical scavenger here. The stannyl radicals resulting from scavenging steps, attack further hydrazine molecules, giving one mole of the stannylamine and, lastly, one mole of diphenylamine[18].
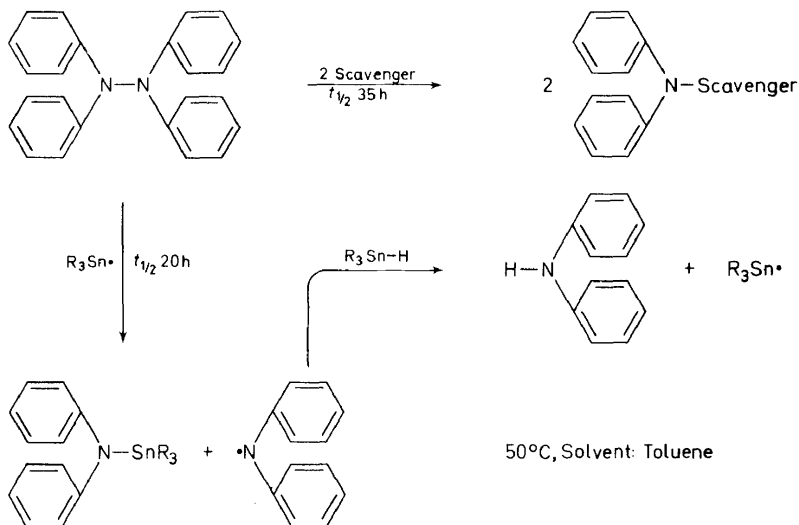
Scheme 15

A peculiar compound is the pentaz-diene[19a], shown in *Scheme 16*. It explodes violently at elevated temperature. We tried only once to take its melting point. But, at low temperature, it behaves quite nicely and can be investigated without trouble. The central nitrogen atom is of special interest here. It is influenced twice by the strongest electron-withdrawing group, the azo group. Therefore, its π-electron density must be very low, and an attack of the nucleophilic stannyl radical should be favoured. In fact, this can be observed[20].

The half-life time drops drastically from 1 830 to about 60 min, depending on the R_3Sn—H concentration. The resulting N-stannyltriazene (or N-stannyldiazoaminobenzene) is remarkably stable and can be distilled *in vacuo* without decomposition. Perhaps, there is pentacoordination around the tin atom, with the azo group working as donor. But, further investigation going on in the Dortmund Laboratories will possibly resolve this problem

$-10°C$ in toluene; $t_{1/2}$ spont. 1830 min, $t_{1/2}$ ind. 60 min
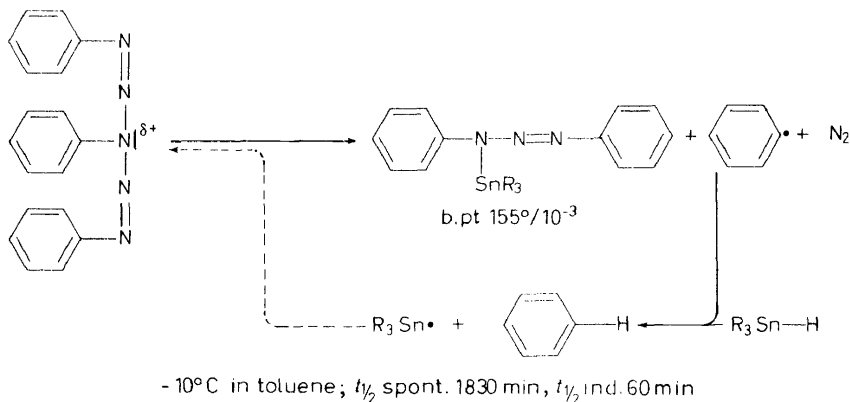
Scheme 16

fully. Stannyl radicals needed for the experiments referred to have been produced from organotin hydrides within the reaction mixture. Often it is advantageous to have these hydrides present for scavenging short-lived radicals, as could be seen from several examples shown above.

It is evident that investigation of stannyl radicals is not only useful for learning more about organic derivatives of group IV B, but also of interest for the chemistry of free radicals in organic chemistry.

ACKNOWLEDGEMENT

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