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Review

Tin for organic synthesis

VI *. The new role of organotin reagents in organic synthesis **
Part 1: Stannyl groups as leaving groups in electrophilic substitutions
Part 2: Polymer-supported organotin reagents for organic synthesis

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Introduction

There has been a considerable growth in interest in recent years in the use of organotin compounds in organic synthesis [2] but there is little doubt that only a small fraction of the potential of such use has yet been realized. This review presents below brief surveys of the recent contributions of the author's group in two areas of this field, involving work based on the extensive experience of the group in organotin chemistry.

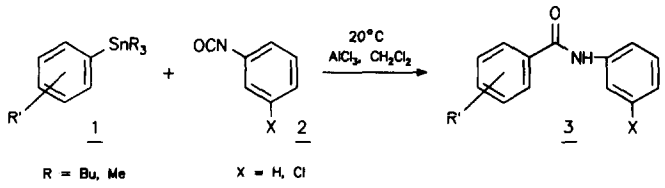
Part 1: Stannyl groups as leaving groups in electrophilic aromatic substitutions (S_Ear)

1.1. General

After demonstrating the use in systhesis of cleavage of aryl-silicon bonds by electrophiles, Eaborn showed that the much greater ease of cleavage of aryl-tin bonds could also be exploited successfully in synthesis, *e.g.* in the introduction of COR, NO (and hence NO_2), CN, SO_2Ar, and Br substituents in place of the $SnMe_3$ group (*ipso*-substitution) by reaction with $RCOCl/AlCl_3$, NOCl, CNCl, $ArSO_2Cl$, and Br_2, respectively [3]. Others showed that NCS and SR substituents could be introduced analogously [4]. Through such reactions the substituents can

* Dedicated to Professor Alwyn G. Davies in recognition of his important contributions to organometallic chemistry. This review is based on a lecture delivered in the University College London, June 28, 1991, in honour of Professor A.G. Davies.

** For Part V, see ref. 1.



	a	b	c	d	e	f	g	h	i
1, 3, R' =	4-Me	4-Cl	4-Cl	3-Me	3-Me	2-Et	3-Cl	3-OMe	3-OMe
3, X =	H	H	Cl	H	Cl	H	Cl	H	Cl
Yield, %	89	81	78	87	88	72	86	75	96

Scheme 1. Electrophilic carbo-destannylation: a new route to substituted aromatic *N*-phenylamides.

be directed into positions not accessible by direct electrophilic substitution involving replacement of hydrogen. We have greatly extended the scope of such reactions by using a wider range of electrophiles.

1.2. ipso-Substitutions of arylstannanes

We first looked at cleavage by Friedel–Crafts acylation reagents. Using $MeCOCl/AlCl_3$ we confirmed Eaborn's observation [5] that fair to good yields of *ipso*-substitution products could be obtained [6]; *e.g.* even in the case of 3-$MeC_6H_4SnMe_3$, in which the positions *ortho* and *para* to the tin atom would be specifically activated towards the replacement of hydrogen.

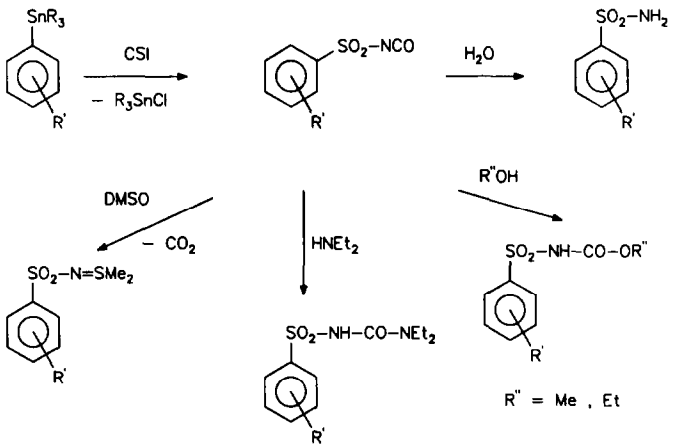
The Vilsmeier reaction, accepted as "the most common method for the formylation of aromatic rings" [7], was previously restricted to highly activated aromatics. Using *ipso*-substitution of a stannyl group we have extended it considerably [6]; *e.g.* a 3-methylstannylbenzene gives the 3-methylbenzaldehyde even at moderate temperatures.

With pure SO_3 at room temperature, the stannyl esters of the corresponding aromatic sulfonic acids are formed in quantitative yields with 100% isomeric purity. Likewise, SO_2 gives quantitative yields of the *ipso*-substitution product very rapidly at room temperature. In both cases, even the strong *ortho / meta* directing effect of a 3-methoxy group is completely over-ruled [6]. Similarly unusually-substituted phenyl *N*-arylamides have been made by carbodestannylation with aryl isocyanates [8]. Only the *ipso*-product is obtained, the yields are excellent, the reactions proceed readily at room temperature, and no excess of the stannyl derivative is needed. The yields shown in Scheme 1 refer to isolated pure products of experiments on a *ca.* 10 mmol scale.

In addition to the *ipso*-regioselectivity the method has a further important advantage. The conventional method, not involving use of tin requires temperatures up to 130°C and a 7–8 fold excess of the aromatic hydrocarbon [9]. Since it takes place under mild conditions the highly selective tin-mediated synthesis should be applicable in the synthesis of high-value natural products or novel biologically-active species [8].

In terms of yields, the much less toxic Bu_3Sn group is as effective as the Me_3Sn group and so normally to be preferred. However, for spectroscopic reasons (^1H NMR) the Me derivatives are also still used in some of our investigations.

Reaction of chlorosulfonyl isocyanate (CSI) with aryltrialkylstannanes provides an efficient route to aromatic sulfonyl isocyanates [10]. The reactions take place



Scheme 2. Electrophilic sulfo-destannylation: a new route to sulfonamides, sulfilimines, sulfonyl-carbamates and -ureas.

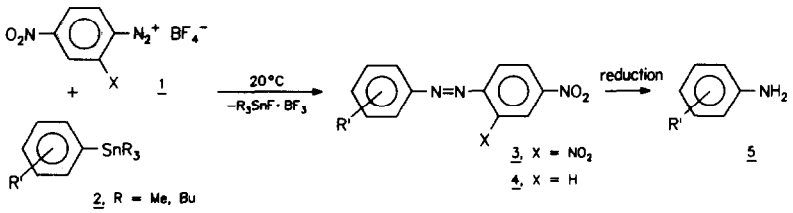
smoothly at room temperature without any catalyst, and lead exclusively to *ipso*-substitution. In the usual method, involving deprotonation, $AlCl_3$ is needed as catalyst, and only highly activated aromatics, *e.g.* those with one MeO group [11*], underwent reaction, with the regioselectivity determined in the usual way. Moreover, in those reactions the products after hydrolysis were the carboxamides, showing that the attack was by the activated isocyanato group [11*]. In contrast with the tin compounds, the CSI reacts, surprisingly, at the Cl–S bond; *i.e.* the CSI behaves in this case like an acyl halide (See Scheme 2).

An important advantage of the new procedure is that sulfonyl isocyanates need not be isolated, but can be transformed *in situ* to valuable products: by an alcohol to the sulfonyl-carbamate, by an amine to the sulfonylurea, by water to the sulfonamide, by DMSO to the sulfilimine. We emphasize again that the approach makes available unusually-substituted species. The yields of isolated pure compounds are fair to excellent (66–98%, in small-scale experiments), and no by-products have been detected.

In reaction with CSI the parent compounds R_3SnPh react smoothly; the deactivating effects of halogeno substituents are overcome, as are the orientating effects of 3-Me or 3-Cl groups. Even the 3-CF_3 derivative undergoes *ipso*-substitution of the stannyl group, and only the CN and the 2-CF_3 substituents prevent the reaction taking place.

A particularly impressive example of the value of the tin compound is shown by the reaction with a very weak nucleophile that in conventional deprotonations reacts only with strongly activated aromatics such like phenols, phenol ethers or amines, namely the diazonium cation. Nitrobenzene-diazonium cations react smoothly and slightly exothermally with trialkylarylstannanes even at room temperature [1]. The arylstannanes are completely consumed and the *ipso*-product is obtained exclusively. The yields shown in Scheme 3 refer to isolated pure products

* Reference number with asterisk indicates a note in the list of references.



	a	b	c	d	e	f	g	h	i	j	
3, R' =	H	2-Me	3-Me	4-Me	4-Et	Mes	2-OMe	4-OMe	4-$SiMe_3$	4-Cl	X = NO_2
Yield, %	31	53	67	62	54	65	16	57	36	14	
4, R' =	–	–	–	–	–	–	2-OMe	4-OMe	–	–	X = H
Yield, %	–	–	–	–	–	–	66	83	–	–	

Scheme 3. Electrophilic aromatic amino-destannylation: new, regioselective, azo couplings.

of small-scale experiments after (often troublesome) chromatographic removal of minor, but strongly-coloured, by-products.

The aromatic diazenes, often not accessible by normal azo coupling, can be valuable reagents for further preparations; for example of aromatic amines with unusual substituent patterns as shown in Scheme 3. In the case of a competition between a silyl and a stannyl substituent as leaving groups, the latter wins clearly as would be expected [3]. For example, **3i** was exclusively obtained, and there was no cleavage of the aryl–$SiMe_3$ bond. Thus the stannyl group is displaced at least 10^2 times as readily as the silyl group by the electrophile.

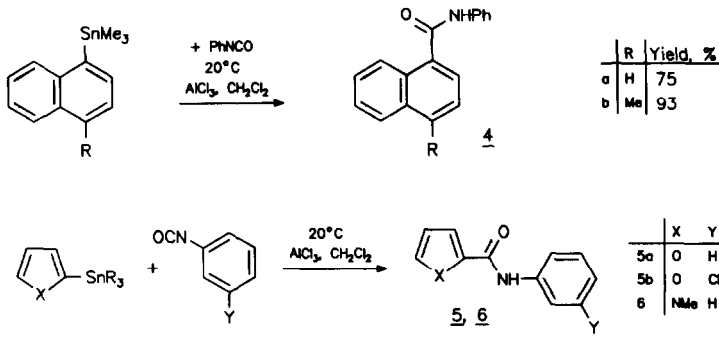
It is noteworthy that 2- and 4-OMe stannylbenzenes undergo only *ipso*-substitution and very quickly, but in the case of the 3-OMe derivative, although the stannyl substituent enhances the overall rate, the OMe group determines the regioselectivity [12], the *para*-product being formed. The 3-Me_2N substituent behaves similarly.

1.3. ipso-Substitutions with stannylated poly- and hetero-aromatics or other unsaturated systems

To gain insight into the scope of the new tin-mediated electrophilic substitutions benzene derivatives were initially used. Clearly the approach should also apply to poly- and hetero-aromatic systems; only a few studies have so far been carried out but the results are encouraging.

α-Trimethylstannylnaphthalene reacts with phenyl isocyanate under mild conditions to give a high (isolated) yield of the *ipso*-product regioselectively (Scheme 4). Naphthalene itself gives only a 16% yield under the same conditions [8]. 2-Trialkyl-stannylfuran and -*N*-methylpyrrole likewise yield the corresponding carbonamides [8].

α-Tributylnaphthalene also reacts with CSI, to give the expected *ipso*-product (Scheme 5), whereas the naphthalene itself gives no substitution products under similar conditions. Remarkably, exclusive *ipso*-substitution also occurs with the less reactive 2-stannyl compound. This overruling of the usual regioselectivity and chemoselectivity by the *ipso*-directing ability of the stannyl group is also found with thiophene [13].



	R	Yield, %
a	H	75
b	Me	93

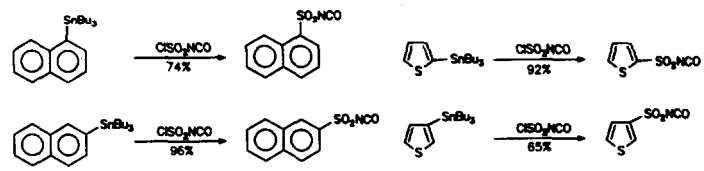
	X	Y	Yield, %
5a	O	H	87
5b	O	Cl	85
6	NMe	H	88

Scheme 4. Electrophilic carbo-destannylation: a new route to substituted aromatic *N*-phenylamides.

With diazonium ions at 20°C, the 1-stannylnaphthalene gives only the 1-diazene, and the 2-stannyl isomer only the corresponding 2-diazene [1].

Less information is available on the role of stannyl groups in electrophilic substitutions at other multiple bonds. Vinyl and alkynyl stannanes are easily prepared, however, [2] and an exploratory study has shown that acyclic, cyclic, and alkynyl carbonamides are easily accessible through the new approach [8] (Scheme 6).

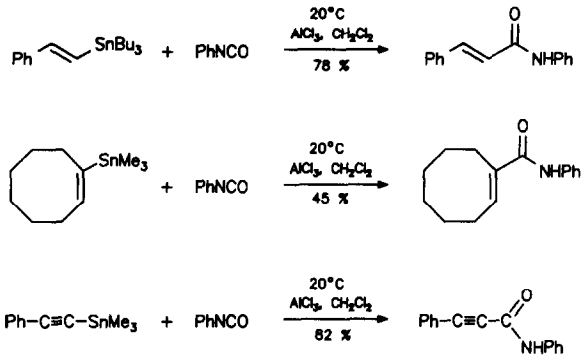
No excess of electrophilic reagent is needed; indeed, when an excess of isocyanate is used the stannylalkyne forms hydantoins [14]. Of course, more research work on these reactions is needed.



Scheme 5. Electrophilic sulfo-destannylation: a new selective route to poly- or hetero-aromatic sulfonylisocyanates.

1.4. Importance of coordination to the tin atom

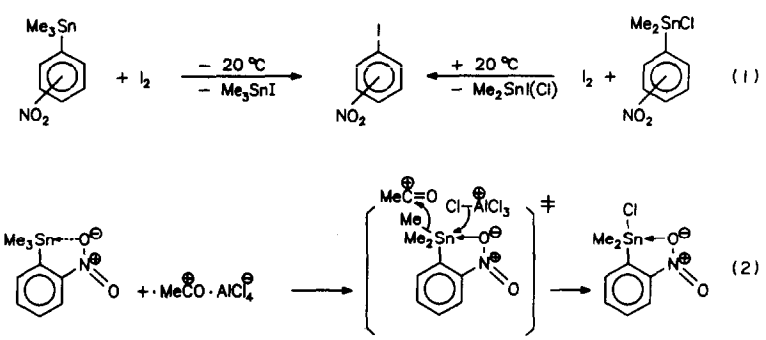
What is the reason for the great ease of these electrophilic substitutions? The fact that the Ph–$SnEt_3$ bond is cleaved by acid *ca.* 10^9 times as readily as the Ph–H bond has been attributed to the powerful hyperconjugative electron-release from the C–$SnEt_3$ bond [3], but we think that at least in some cases precomplexation of the attacking reagent with the tin atom probably plays an important role. We did not detect any intermediates that would support this hypothesis in the case of the reactions described, but a surprising insight was offered by an unexpected observation, namely that whereas 2-nitrostannylbenzene is attacked by iodine in the normal way, (reaction 1 in Scheme 7), the weaker Friedel–Crafts electrophile $MeCOCl/AlCl_3$ only cleaves one of the (normally rather stable) Me–Sn bonds [15]. The aryl–Sn bond, usually much more sensitive, remains intact. This reaction might be understood in terms of the process shown in eq. 2 in Scheme 7 [15].



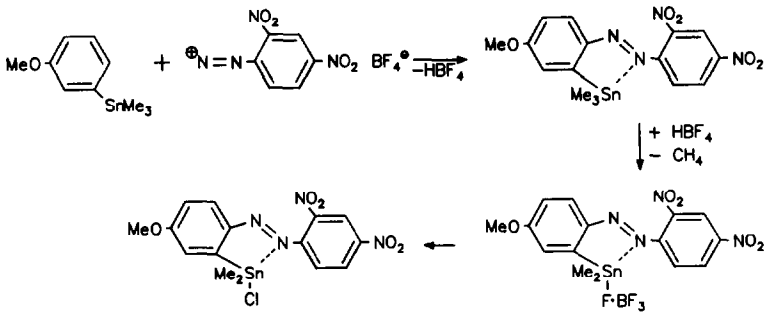
Scheme 6. Electrophilic carbo-destannylation of alkenes and alkynes: a new route to substituted *N*-phenylamides.

In this case the attacking species, which is both an electrophile and a nucleophile, can neither displace the stannyl group (for of steric and energetic reasons) nor escape by diffusion after fruitless attack. Thus, what normally is probably only a transition state becomes a stable species in this case. The compound under attack is a tetraorganotin, and although it has long been assumed that such species can form complexes as a result of extra-coordination at the tin atom there was no direct evidence for such complexes. Recently, however, such a complex was shown in the solid state by X-ray analysis [16], others have been observed in solution [17]. Coordination to tin has been very recently observed in the products from the reactions of 3-MeO- and 3-Me_2N-(trimethylstannyl)benzene with a diazonium ion, where the regioselectivity is governed by the MeO or NMe_2 group, as in Scheme 8 [12].

The final product is crystalline [12], and a very short Sn–N distance of 2.674 Å was revealed by X-ray crystallography [18]. It is surprising (since there are two nitro substituents on the adjacent phenyl residue) that the donor nitrogen atom in the diazene can enter into such strong bonding. This is evidence for coordination, to be used in the discussion below.



Scheme 7.



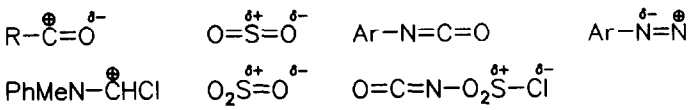
Scheme 8.

1.5. Mechanistic consideration and conclusions

We have seen above that a variety of electrophiles can bring about *ipso*-substitution of aryltrialkylstannes. However, not all do so, and in particular Friedel–Crafts alkylation reagents bring about no *ipso*-substitution [6,19].

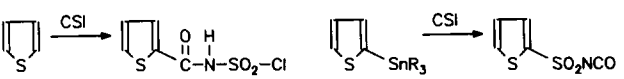
Kinetic investigations suggest that the mechanism of electrophilic carbon–tin cleavage might involve either a cationic Wheland-intermediate [3] or a four-membered transition state [3,20*]. In some cases, the cationic species seems to be a poor approximation to the actual transition state, but the kinetic data do not allow a definite choice between the alternatives. We consider that both mechanisms should be possible, depending on the electrophilic species, choice of solvent, *etc.*

All the electrophiles mentioned above that bring about *ipso*-substitution have at least one donor atom adjacent to the electrophilic site, whether in a cation or a neutral multibonded species.



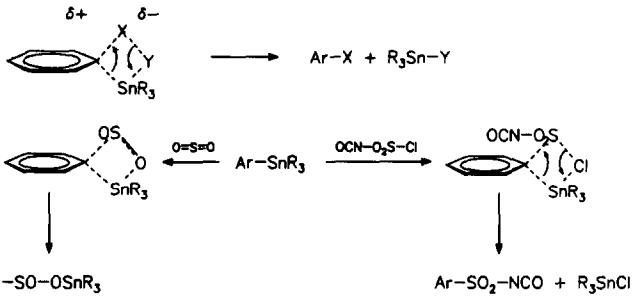
Taking into account the acceptor ability of the tin atom in (demonstrated in Section 2.4) and the donor ability of the unsaturated system, a four-membered cyclic transition state offers a reasonable explanation of the very high (usually exclusive) *ipso*-substitution, the enhanced rate, and the reverse chemoselectivity in the reaction of CSI with aryltrialkylstannanes. Some examples that support this view [20*] are shown in Scheme 9.

Furthermore, thiophene reacts with the electrophilic centre of CSI, whereas its stannyl derivative reacts at the S–Cl bond:



Moreover, with *meta*-methoxyarylstannanes, exclusive *ipso*-substitution occurs in amidation (because of the high donor ability of the electrophile) but not in acylation [8].

In the cases so far studied, the most stable tin compound (as indicated by the following bond dissociation energies (in kcal/mol): Sn–C_{ar} ≈ 60, Sn–O ≈ 85, Sn–



Scheme 9.

N ≈ 70, Sn–Cl ≈ 85) is always formed. Cleavage of the stannyl moiety from the aromatic nucleus is always clearly exothermal, and this provides a specific additional driving force for the cleavage.

We have shown that use of the very high leaving group ability of the trialkylstannyl group in electrophilic substitutions enables high yields of *ipso*-substitution products to be obtained under mild conditions, even with weak electrophiles. At present the work of this group is being directed toward lowering the molar amounts of tin that have to be used, *i.e.* to using one tin moiety as leaving group from more than one unsaturated fragment by starting from organotin compounds bearing more than one (appropriately-substituted) aromatic or other unsaturated groups on the tin atom. An even more exciting prospect is opened up by our plan to use polymer-supported organotin starting materials, where the tin moiety would remain on the polymer after electrophilic substitution, and be available for regeneration. An appropriate system would be of the type polymer-Bu_2Sn–aryl + X–Y → aryl–X + polymer–Bu_2Sn–Y. Some of the pre-requisites for being able to do this are outlined in Part 2.

Part 2: Polymer-supported organotin reagents for organic syntheses

2.1. General consideration

Most of the reactions described below involve free radicals. For a long time these were regarded as very reactive (often too reactive) but unspecific, but they have recently been shown to be highly specific and extremely stereoselective. Stannyl radicals $R_3Sn^{\cdot}$ and organotin hydrides R_3SnH, the latter usually serving as precursors for the former, are much involved in this remarkably rapid development. The following quotations are relevant: (a) "Within the last 15 years, an authentic explosion of synthetic applications of free radical reactions occured; they have gained a remarkable position among the selective methods of synthesis" [21]; (b) "The dramatic advances in the application of free radical reactions to problems in organic synthesis can be attributed in good measure to the versatility of trialkytin hydride reagents" [22]; (c) "The reduction of organic functional groups by organotin hydrides ... has become the most commonly used method for the synthetic application of free radical carbon–carbon bond formation" [23]; (d) "Perhaps no aspect of chemistry has developed faster in the last 2–3 years than radical ring closure, conventionally terminated by H-atom transfer from tri-n-butyltin hydride" [24]. This last reagent in particular is now much used [25].

Multistep-one-pot reactions (tandem reactions) can be carried out very easily. The yields are high or quantitative and often show complete chemo-, regio-, stereo- and/or enantio-selectivities, especially in ring closures [23,25–27]. The progress made was based largely on earlier kinetic [28] and mechanistic studies [29] of free radical mode reactions, which were then shown to be useful in a broad sense, as were the basic organotin radical reactions which were observed as early as 1961 [30].

Sometimes, the organotin hydride is a too powerful scavenger for radicals, so that it inhibits slow steps involving intermediate radicals in chain reaction such as ring closures or intermolecular additions. In such cases other sources of stannyl radicals $R_3Sn^{\cdot}$ have been recommended, such as distannanes R_3SnSnR_3, bisstannyl benzpinacols $R_3SnOCPh_2CPh_2OSnR_3$, and certain benzylic [6,31] or allylic [2,27] tin compounds. Both thermal and photolytic initiation is available [6,31].

However, there is a considerable disadvantage in the use of these stannyl radical sources, especially for the preparation of biologically-active or pharmaceutical products, and this is the problem of separation of organotin byproducts from the desired reaction products; this separation "is mostly a difficult, and rarely a quantitative one. It might be, therefore, a meritorious research project to find new methods using forms of organotin compounds that can be easily separated" [32].

We initiated such a project by preparing a series of polymer-supported tin reagents. The idea is to bind the tin reagent in a very stable position to an insoluble porous polymer which can be separated after the reaction simply by filtration. It should also be possible to regenerate the tin reagent itself, allowing multiple use.

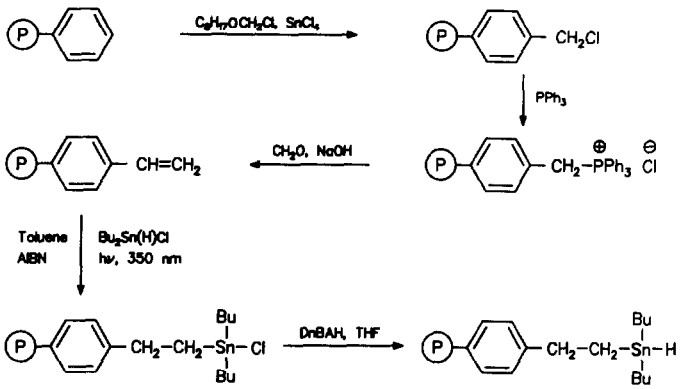
Economic and ecologic considerations at present provide a strong stimulus for development of polymer-supported reagents and catalysts in general [33–45], and led to the first international symposium on "Supported Reagent Chemistry" [35]. Only a few studies have involved polymer-supported organotin compounds [36–39], and in these various carriers have been tried.

2.2. Syntheses of polystyrene-supported organotin hydrides

We selected as the polymer carrier a cross-linked macroporous polystyrene with sufficient porosity, involving large and open pores. This material seemed most suitable because of its insolubility in most common solvents, its low tendency to swell, its high mechanical and chemical resistance, its uniform structure, and last but not least, its very low tendency to adsorb other materials, for example the reaction products.

Thus, we subjected commercial polystyrenes to Wittig vinylation followed by hydrostannation using the very reactive chlorohydride $Bu_2Sn(H)Cl$ (see Scheme 10). We were experienced in handling this very reactive species from earlier work [40]. The way ahead was long and tedious, with many failures and surprises – even for professional polymer chemists, and we were amateurs in the field in those days [41]. Among others, a special problem was to find the best reducing agent for the resulting tin chloride.

One of the surprises came during the search for the best degree of functionalization. The highest value is not necessarily the best. On the contrary, there is a specific dependence on the type of the polystyrene used, with an individual optimum, as shown in Fig. 1 [42,43], and this should not be exceeded. Another



Scheme 10. Functionalization of a suitable polystyrene.

unpleasant surprise was the initial tin content of the effluent THF, which was reduced to zero only after extensive washing (see Fig. 2). It turned out that oligomers of the gel type (with little or no crosslinking), which had been functionalized by our method, escaped slowly from the resin, see Fig. 1 [42]. Careful prolonged washing had to be carried out before functionalization of the resin.

Thus, a second method was developed, starting from divinylbenzene (DVB), which after mono-hydrostannation by $Bu_2Sn(H)Cl$ was polymerized by cross-linking with divinylbenzene itself. No additional (unsubstituted) styrene was added [41–43] (Scheme 11).

For the results shown in Scheme 12, we used a functionalized polystyrene resin with a measured content of active Sn–H bonds of 1.2–1.4 milli-equivalents per gram. Regeneration for multiple use was not a problem: after 7 application–regeneration cycles using n-octyl bromide as a test compound there was no measurable

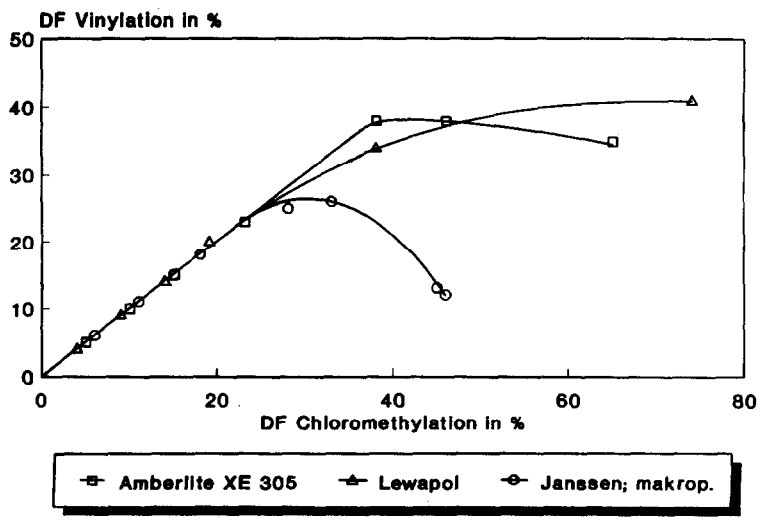
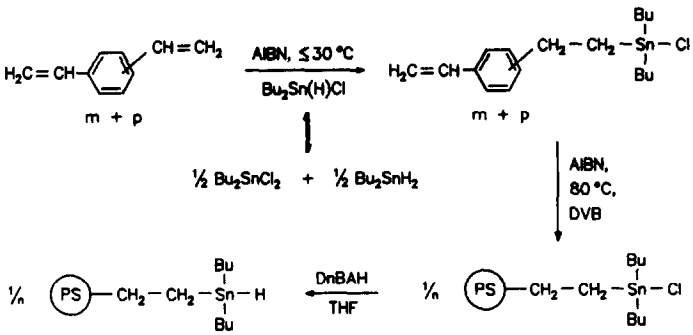


Fig. 1. Vinylation of polystyrene resins.



Scheme 11. Polymerization of a functionalized momomer.

decrease in the active Sn–H content [44]. Thus, a reactive resin is now available for practical use.

2.3. Free radical syntheses by use of polymer-supported organotin hydrides

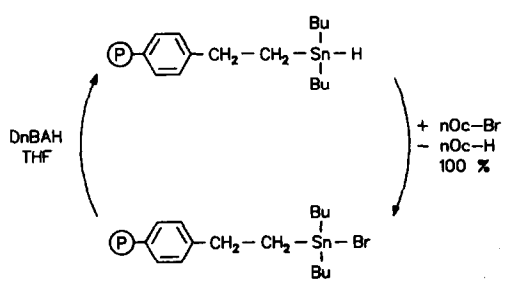
To check the practical value of the new hydride reagents, we used three of the most important, most frequently used free radical reactions [23–26,45]: dehalogenation (also important after atom-transfers [46]) of chlorides and bromides, dehydroxylation of secondary alcohols involving olefin formation, and deaminations of secondary and tertiary amines. Such reactions had previously been carried out with Bu_3SnH [25,47–51], and so were appropriate for testing the polymer-supported reagent (see Schemes 13–18).

The yields shown refer to isolated pure compounds (unless otherwise stated) in 1–5 mmol experiments. Conversion was complete in each case, and neither side-products nor losses by adsorption were detected (GLC, 1H NMR, mass balance) [42–44]. Work-up simply involved filtering off the resin, washing it, and evaporating the solvent. The resin was then ready for regeneration.

In all cases so far studied the polymer-supported tin hydride fully matches Bu_3SnH in reactivity and selectivity [25,45] under similar, mild, conditions. Of course, more time, but surprisingly little more [44], has to be allowed for the diffusion-controlled chemistry inside the polymer beads.

2.4. Other polymer-supported organotin reagents

Organotin hydrides are sometimes not to be recommended as sources of stannyl radicals, since, as mentioned in Section 2.1 above, they are too efficient as radical



Scheme 12. Test of multiple use of the reactive polymer after regeneration.

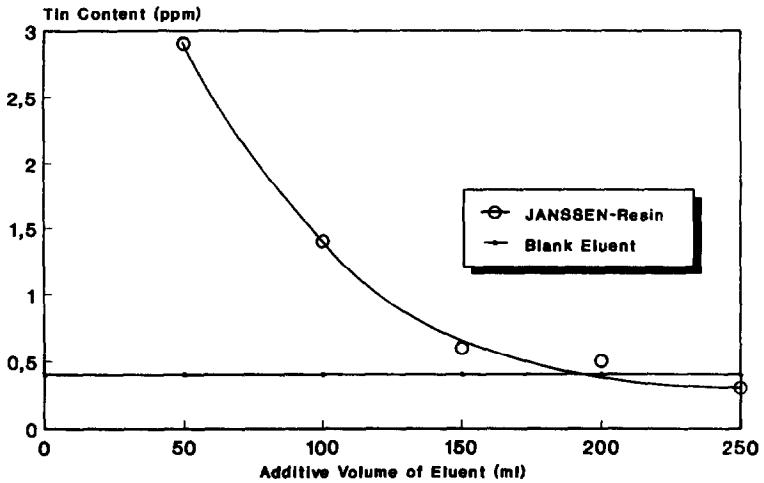
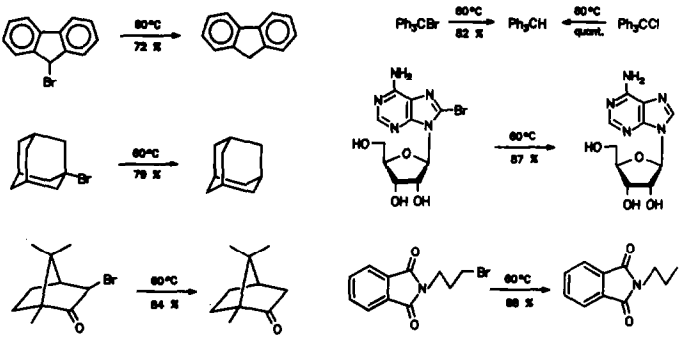
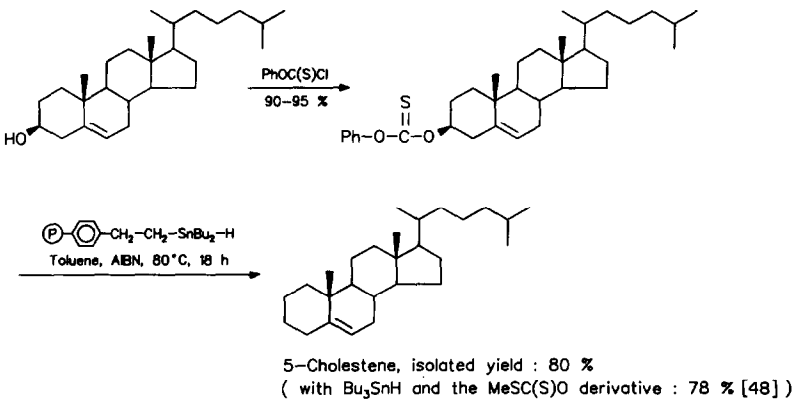


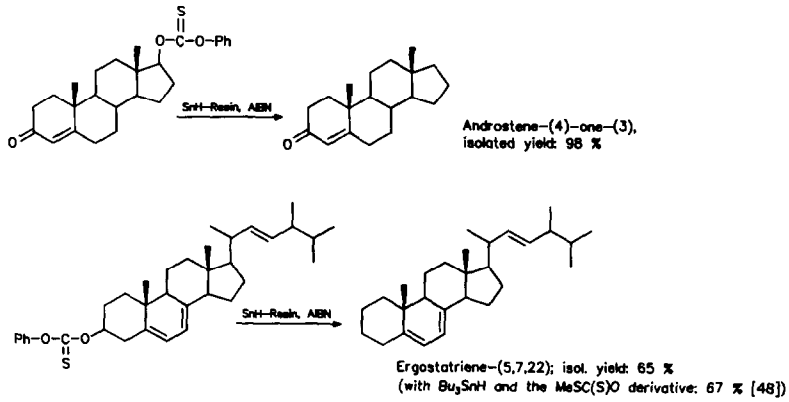
Fig. 2. Tin atomic and absorption analysis: tin eluted with THF from a resin containing 14.8 mmol tin chloride.



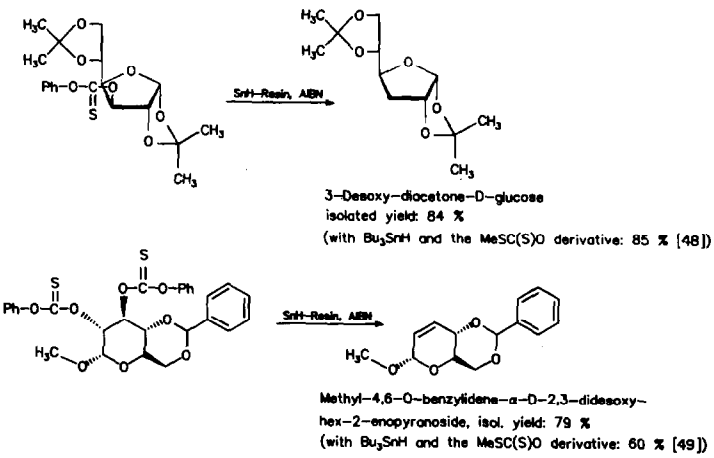
Scheme 13. Model dehalogenations with a polymer-supported tin hydride.



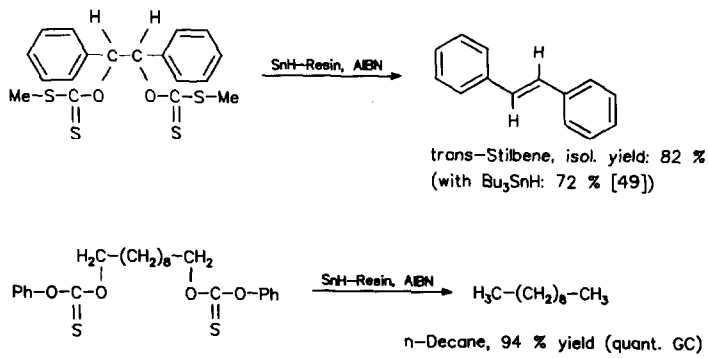
Scheme 14. Barton-type deoxygenation with a polymer-supported tin hydride.



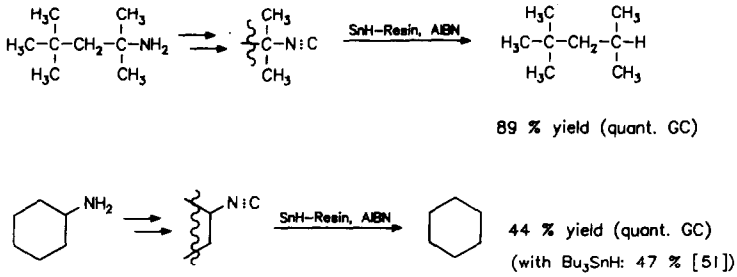
Scheme 15. Barton-type deoxygenation of steroid derivatives.



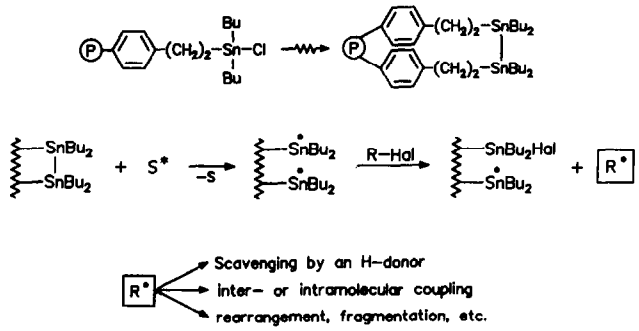
Scheme 16. Barton-type deoxygenation of sugar derivatives.



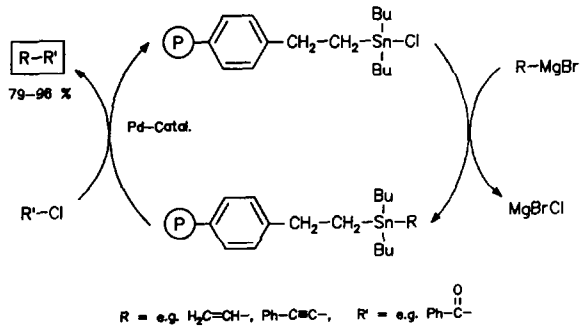
Scheme 17. Barton-type deoxygenation of diols.



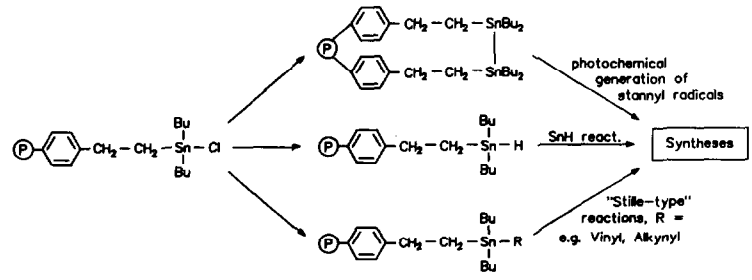
Scheme 18. Barton-type deamination of sec- and tert-amines.



Scheme 19. A polymer-supported distannane as a source for carbon radicals.



Scheme 20. C-C couplings of the Stille-type with polymer-supported organotin reagents.



Scheme 21. Synthesis using polymer-supported tin compounds.

scavengers. In order to promote slow but desired reactions of the intermediate radicals, a polymer-supported distannane would be desirable, to be used along with an appropriate, relatively weak H-donor such as THF, if necessary. A species having a distannane with both of its tin atoms bound to the polymer has indeed been developed [42,43,52], (Scheme 19), and its practical application is under investigation.

An attractive extension of the Stille reaction [14], the C–C coupling between an organic halide and a stannylated vinyl or other unsaturated compound, would involve immobilization of the latter on a polymer and recycling of the tin reagent. This can be done with our polystyrene-support butyltin chloride (Scheme 20) [42,43].

2.5. Outlook and conclusions

Starting from the polystyrene-supported organotin chloride described in Section 2.2, a set of valuable organotin reagents for organic syntheses has been developed as summarized in Scheme 21.

The applications shown are just examples. Future developments can be expected, such as the use of the chloride itself as catalyst for olefin isomerizations, a polymer-supported version of the copper-mediated tin hydride reactions, and so on, involving either free radical or non-radical mechanisms. Some of them are under investigation in our laboratory.

In summary, use of our polymer-supported reagents has the following advantages: (a) easier processing than with monomeric reagents, (b) simple and clean work-up of the products by filtration, (c) avoidance of problems with organotin waste, and (d) availability of regeneration of the reagent for multiple use. We are hopeful that a new branch has been added to the flourishing tree of applications of organotin compounds in synthesis.

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