Nitration of Heteroaryltrimethyltins by Tetranitromethane and Dinitrogen Tetroxide: Mechanistic Aspects, Scope and Limitations

Valérie Fargeas,[a] Fabien Favresse,[b] Didier Mathieu,[b] Isabelle Beaudet,[a] Pierre Charrue,[b] Bruno Lebret,[b] Marc Piteau,[b] and Jean-Paul Quintard*[a]

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The nitration of 2-(trimethylstannyl)heteroarenes by tetranitromethane (TNM) or dinitrogen tetroxide has been shown to be possible when the HOMO energy of the heteroaryltin is high enough to allow the formation of the corresponding radical cation. The reaction proceeds through a charge-transfer complex between heteroaryltin and TNM, followed by a single-electron transfer, which is enhanced under sunlamp irradiation. Accordingly, 2-nitrobenzo[*b*]furan, 2-nitrobenzo[*b*]thiophene, 2-nitropyridine and 2-nitroindoles were obtained by this method. However, the nitration of 2-stannylated pyrimidine or of stannylated 1,3,5-triazines has been shown to be impossible, due to the low energy of their HOMO orbitals.

Introduction

Research developments in the field of high-energy materials (explosives) have in recent years focussed on the improvement of the properties of conventional explosives such as nitroglycerine, trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), hexogen (RDX), octogen (HMX) or 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The desired improvements may concern the explosive power of the new materials and for this purpose the values of ΔH_f (enthalpy of formation), density and oxygen balance have been shown to have crucial importance for explosive and detonative properties.[1−6] While oxygen balances of zero (or slightly negative) result in an increase in the force and pressure of an explosion, the design of strained systems can introduce additive energy.[7] This approach has been exploited to obtain strained nitroamine derivatives such as sorguyl[8,9] or HNIW[10,11] and very recently to obtain octanitrocubane.[12]

Obviously, the explosive power has to be combined with safety-related properties (moderate sensitivity to impact or friction) and for this purpose predictive methods taking these two properties into account have been developed. Studies concerning impact sensitivity[13−15] in combination with the predictive CARTE method for energetic properties[16,17] suggest that pernitropolyazaheterocycles such as 3,4,6-trinitro[1,2,4]triazolo[4,3-*a*][1,3,5]triazine might be good candidates. With a slightly negative oxygen balance, this compound is expected on the basis of theoretical calculations to have a density near 2 and a detonation speed close to 9700 m·s^{-1}.[18,19]

At this stage, the main problem remains the synthesis of the title compound, and initial attempts starting from 3,4,6-triamino[1,2,4]triazolo[4,3-*a*][1,3,5]triazine or [1,2,4]triazolo[4,3-*a*][1,3,5]triazine were unsuccessful. Furthermore, in the second case, the [1,2,4]triazolo[4,3-*a*][1,3,5]triazine very easily isomerizes into the more stable [1,2,4]triazolo[1,5-*a*][1,3,5]triazine.[20]

Empirical calculations performed on [1,2,4]triazolo[4,3-*a*][1,3,5]triazine and [1,2,4]triazolo[1,5-*a*][1,3,5]triazine by an AM1 method demonstrate low electron densities on the three carbon atoms of the bicyclic systems in both cases, the least disfavoured carbon in each case being that of the five-membered ring. In any case, nitration reactions in heteroaromatic series under conventional electrophilic conditions are highly disfavoured due to the presence of heteroatoms.[21] One possible way to improve the reactivity of such heterocycles might be by the use of tris(trimethylsilyl) or tris(trimethylstannyl)triazolotriazines, which might furthermore also bring improvements in terms of solubility.

Because of the absence of results for synthesis and nitration of such structures in the literature, we decided to examine the influence of silyl or stannyl substitution on much simpler structures, as described below.

Results and Discussion

I. Choice and Synthesis of the Model Molecules

In a first step, we decided to examine the reactivities of metallated heterocycles containing only one heteroatom,

[a] Laboratoire de Synthèse Organique, UMR 6513 du CNRS, Faculté des Sciences et des Techniques de Nantes,
2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France
Fax: (internat.) + 33-2/51125412
E-mail: quintard@chimie.univ-nantes.fr
[b] CEA Le Ripault
BP 16, 37260 Monts, France

both in a six-membered ring (silylated or stannylated regioisomers of pyridines **1**−**3**) and in a five-membered ring (stannylated benzo[*b*]furan **4**, benzo[*b*]thiophene **5** or indoles **6** and **7**) and subsequently to evaluate the reactivities of compounds containing two or three nitrogen atoms in the six-membered ring, such as 2-(trimethylstannyl)pyrimidine (**8**) or 2,4,6-tris(trimethylstannyl)-1,3,5-triazine (**9**) (Figure 1).

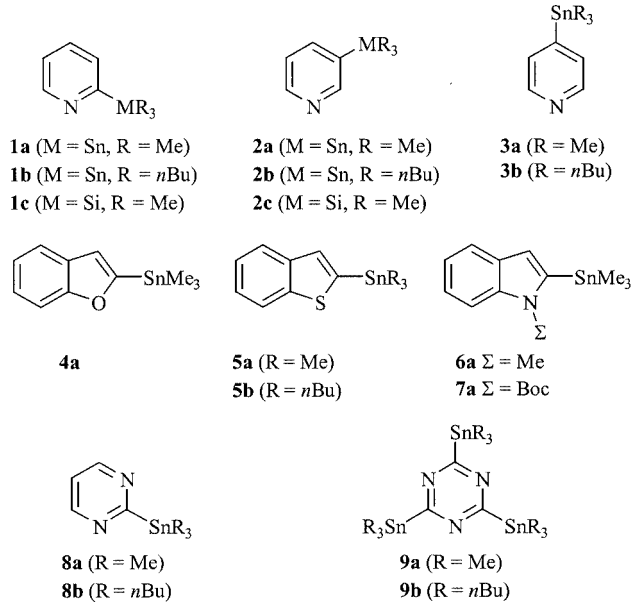
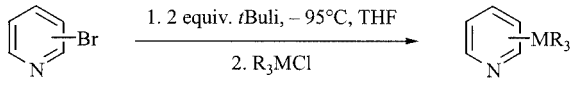


Figure 1. Selected silylated and stannylated heterocycles

The preparation of the above species might be approached through the use of heteroarylanions obtained by direct metallation of the heterocycle,[22,23] by halogen−metal exchange[24−27] or by synthesis of the appropriate Grignard reagent in situ.[28−30] However, such approaches require substrates fairly insensitive to strongly basic experimental conditions and are therefore limited to compounds **1**−**5**. A milder procedure might be the use of triorganosilyl or triorganostannyl anions, which have previously been employed to achieve syntheses in the pyridine series[31,32] and the pyrimidine series.[33,34] However, these reagents are prone to give side products, due to the existence of several reaction mechanisms.[35] A more attractive route in terms of mildness of experimental conditions is undoubtedly the cross-coupling of halogenated heterocycles (X = I or Br) with hexamethylditin under catalysis by palladium complexes.[34,36−39] Here again, though, Stille cross-coupling between the initially obtained heteroaryltin and the heteroaryl halide[40] is responsible for the formation of biheteroaryl derivatives.

In practice, when tested in the tributyltin series on 3-bromopyridine, halogen/metal exchange with *t*BuLi in THF at −95 °C and subsequent quenching with tributyltin chloride at −90 °C affords 3-(tributylstannyl)pyridine in 58% isolated yield, slightly higher than the yields obtained by use of Lee's method[30] or of (trimethylstannyl)lithium.[31] Accordingly, the halogen/metal exchange procedure was used to obtain the desired stannylated or silylated pyridines (Scheme 1).



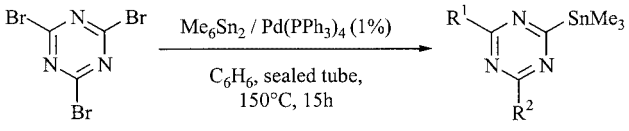
Scheme 1. Preparation of silylated and stannylated pyridines

For the stannylation of the 2-position of benzo[*b*]furan, benzo[*b*]thiophene or *N*-substituted indoles, the previously described deprotonation of these substrates with *n*BuLi and subsequent quenching with triorganotin chlorides allows efficient access to **4a** (78% yield),[41,42] **5a** and **5b** (82 and 86% yields)[43], **6a** (78% yield) and **7a** (37% yield).[44]

In the pyrimidine series, the 2-stannylpyrimidines were obtained by Undheim's method,[33] by treatment of 2-chloropyrimidine either with (tributylstannyl)lithium in THF at −80 °C (**8b**, 61% yield) or with (trimethylstannyl)sodium in DME at 0 °C (**8a**, 27% yield).

The problems arose when the synthesis of **9b** was attempted. Unusable mixtures of compounds were obtained upon treatment either of cyanuryl chloride or 2,4-dichloro-6-phenoxy-1,3,5-triazine with (tributylstannyl)lithium in THF at 0 °C, −40 °C, −80 °C, and −90 °C. Among the numerous compounds detected by GC-MS, the occurrence of a signal with the fragmentations expected for tributyltin cyanide seems indicative of cleavage of the triazine heterocycle, which might be due to the basicity of the organometallic reagent.

To circumvent this problem, taking into account that Stille cross-coupling has previously been achieved on cyanuryl halides,[45] a palladium-promoted reaction between cyanuryl bromide and hexamethylditin was attempted. The bromide substitution resulted in a complex mixture of stannylated triazines from which we were unable to characterise **9a** by GC-MS analysis (Scheme 2).



10 : $R^1 = R^2 = H$; **11 :** $R^1 = Me$; $R^2 = H$; **12 :** $R^1 = R^2 = Me$;
13 : $R^1 = SnMe_3$; $R^2 = Me$; **14 :** $R^1 = SnMe_3$; $R^2 = CN$

Scheme 2. Reaction between cyanuryl bromide and hexamethylditin

Even if not fully identified, triazines **10**−**14** have retention times and fragmentation patterns that might be in agreement with the given structures. These results might be explained by competitive cleavage of the Sn−Sn and Sn−C bonds from hexamethylditin in the transmetallation step, and dehalogenated products might result from a homolytic

pathway. Furthermore, the occurrence of **14** is probably the result of a decomposition reaction allowing formation of trimethyltin cyanide which subsequently engages in Stille cross-coupling.

II. Nitration of Heteroaryltrimethyltins and Related Species

While iododestannylation of stannylpyridines and related compounds through *ipso* substitution has been shown to be a convenient route to the corresponding iodoheterocycles,[31] nothing is known about the electrophilic nitration of these stannylated heterocycles.

The use of nitrosyl chloride (followed by permanganic oxidation) has been shown to be efficient for cleanly obtaining nitro derivatives in strained systems such as 3-(trimethylstannyl)-1,2-dihydrobenzocyclobutene[46] but the higher charge density in such aryltins appears on the stannylated aromatic carbon, thus allowing the *ipso* substitution. In the case of pyridines, however, the higher charge density remains on the nitrogen atom despite silylation or stannylation on the heteroaromatic ring. The subsequent formation of pyridinium salts appears to be highly favoured, with concomitant deactivation of the heteroaromatic ring towards electrophilic substitution. In these circumstances, the failure of the nitration reaction on silyl and stannylpyridines with $Cu(NO_3)_2/Ac_2O$,[47] NO_2Cl[48] or NO_2BF_4[49] is not surprising.[50]

The failure of these reactions was attributed to the electrophilic natures of the reagents. To circumvent this problem, we decided to use stannylated heterocycles in reactions that seemed likely to proceed through initial monoelectronic transfer. Among the results reported in the literature, nitrodestannylation of vinylstannanes[51] and of 2-(trimethylstannyl)benzo[*b*]furans[41] by tetranitromethane (TNM) as well as nitrodemetallation of plumbylpolynitrocubanes by N_2O_4[52] can be placed in this category. We therefore decided to examine the reactivities of heteroaryltins in nitration reaction with these two reagents.

II.1 Nitration of Heteroaryltins with Tetranitromethane and Dinitrogen Tetroxide

II.1.1 Exploratory Results Involving 2-Stannylpyridines

On the basis of Corey and Einhorn's results,[41,51] we decided to examine the possibilities of reactions between 2-triorganostannylpyridines and tetranitromethane under similar experimental conditions (DMSO, 20 °C, 3 h, 1.1 equiv. TNM).[53]

With 2-(tributylstannyl)pyridine (**1b**) as starting material, a 5% conversion rate into 2-nitropyridine **15** was observed (2% isolated yield), without significant improvement being brought by an increase in the reaction time. However, this initial attempt, which appeared to be reproducible, allowed several observations:

1. A deep yellow colour was observed upon addition of TNM to the solution of **1b** in DMSO, changing to orange and brown after two hours.

2. This reaction was completely inhibited by addition of Irganox 1010 (inhibitor of free radical reactions) or by addition of 1,3,5-trinitrobenzene (inhibitor of single-electron transfer, due to its low LUMO energy).

3. Use of 2-(trimethylstannyl)pyridine (**1a**) instead of **1b** allowed a conversion rate near 10% into 2-nitropyridine (5% isolated yield).

On the basis of these preliminary results, **1a** was subsequently used as starting material for attempts directed towards the optimization of the experimental conditions. Since the formation of a charge-transfer complex and a subsequent single-electron transfer was strongly suspected, we decided to examine the effect of light on the course of the reaction, since reactive species were expected to be more easily obtainable with irradiation of the charge-transfer

Table 1. Reaction between 2-(trimethylstannyl)pyridine **1a** and tetranitromethane

Entry	Irradiation system[a][b]	Irradiation time	Solvent (additive)	Yield[c]
1	without	180 min	DMSO (3 mL)	5%
2	Hg lamp	90 min	DMSO (3 mL)	9%
3	Hg lamp	90 min	DMSO (1 mL)	11%
4	sun lamp (150 W)	90 min	DMSO (1 mL)	13%
5	sun lamp (500 W)	90 min	DMSO (1 mL)	22%
6	sun lamp (500 W) + AgCl filter	90 min	DMSO (1 mL)	40%
7	sun lamp (1000 W) + AgCl filter	5 min	DMSO (1 mL)	[d]
8	sun lamp (500 W) + AgCl filter	90 min	CH_2Cl_2 (1 mL)	2%
9	sun lamp (500 W) + AgCl filter	90 min	CCl_4 (1 mL)	15%
10	sun lamp (500 W) + AgCl filter	90 mn	DMSO/CCl_4 (4 mL, 2:3)	23%
11	sun lamp (1000 W) + AgCl filter	45 mn	DMSO/CCl_4 (4 mL, 2:3)	43%
12	sun lamp (1000 W) + AgCl filter	45 mn	DMSO/CCl_4 (4 mL, 2:3) + 1,3,5-trinitrobenzene	5%

[a] The reactions were performed in a Pyrex flask fitted with a reflux condenser with 1 mmol of **1a** (entries 1−9) or 2 mmol of **1a** (entries 10−12). In every case, 2 equiv. of TNM were used as nitration reagent. [b] The Hg lamp or the sun lamp was placed at 30 cm from the flask and the AgCl filter (when used, intercalated at 3 cm from the flask). [c] The yields of 2-nitropyridine **15** were determined by GC-MS analyses after extraction and addition of a standard to the extracted phase. [d] Under these experimental conditions, the cold air blowing system was unable to maintain the temperature of the reaction near 20 °C and an uncontrolled exothermic reaction took place.

complex.[54−56] Preliminary experiments were carried out with 1 mmol of **1a** in 3 mL of DMSO by treatment with 2 equiv. of TNM at 20 °C in a Pyrex flask, and it rapidly became evident that an irradiation time of 1 h 30 min was more convenient than a longer irradiation time and that a temperature near 20 °C was a good compromise (more suitable than 10 °C or 40 °C). The use of a larger excess of TNM (4 equiv.) did not affect the conversion rate, but an increase in the concentration of the reagents (use of 1 mL of DMSO instead of 3 mL) produced a slight increase in the conversion rate into 2-nitropyridine. The details of other attempts are presented in Table 1.

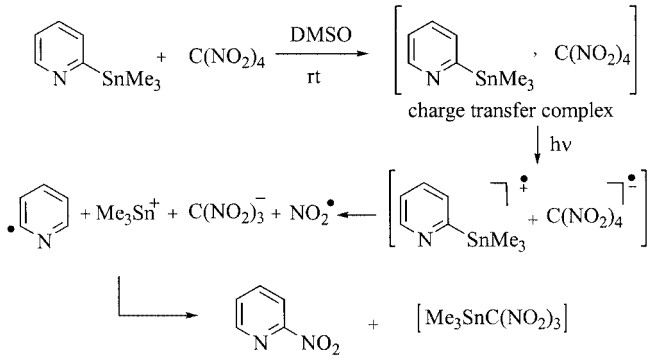
Initially performed with a UV lamp (entries 2 and 3), irradiation was subsequently carried out by use of sun-lamps, with adjunction of a silver chloride filter (in addition to the Pyrex flask). This choice was made on the basis of the UV spectrum of the complex **1a**-TNM, which exhibits two bands at 350 and 425 nm. While the first might be due to nitroform, the second can be attributed to absorption by the charge-transfer complex, by analogy with previous studies involving TNM and aromatics. Accordingly, the key step in this reaction should be photoinduced electron transfer, producing a TNM radical anion and a heteroaryltin radical cation, which requires only irradiation near 425 nm. The use of the AgCl filter (cut off: 400 nm) avoids potentially counterproductive higher-energy excitations that might be capable of inducing side reactions.

The choice was fully justified by an increase in the yield from 22% to 40% (entries 5 and 6). Increased lamp power also seems to be of interest, but the reaction flask could not be cooled enough (by a flux of cold air) under a 1000 W sun-lamp and we were initially unable to control the reaction. To solve this problem, use of a solvent with a low boiling point seemed suitable for maintaining the temperature under 80 °C, and after attempts with dichloromethane and carbon tetrachloride (entries 8 and 9), we made the choice of a mixture of DMSO and CCl_4. Under these experimental conditions, it became possible to control the reaction even under a 1000 W sun-lamp, and a higher yield (43% in crude nitropyridine) was obtained in 45 min.

As far as the reaction mechanism is concerned, it seems reasonable to consider the initial formation of a charge-transfer complex, which has been characterised by UV (vide supra), IR and NMR spectroscopy (cf. Exp. Sect. for characterization of the complex between **1a** and TNM). These data are consistent with a lower charge on the heterocycle in the complex.

With reference to previous studies by Kochi and Eberson[54−58] for the case of aromatic compounds, irradiation of the complex may in our case induce the reaction mechanism summarized in Scheme 3.

The inhibition of such a reaction by Irganox might be explained by free radical trapping, while inhibition by trinitrobenzene might be due to its LUMO orbital being close in energy to that of TNM, possibly allowing competition for the monoelectronic transfer. These different points are discussed in the last section of this paper, after consideration of the reactivity of other stannylated heterocycles.



Scheme 3. Nitration of 2-(trimethylstannyl)pyridine by TNM under irradiation

II.1.2. Nitration of Heteroaryltins by Tetranitromethane or Dinitrogen Tetroxide

From this preliminary study, it appeared reasonable to avoid the irradiation step through the use of a nitration reagent capable of giving nitro radicals more readily, and for this purpose dinitrogen tetroxide might be an appropriate reagent.[59,60] Accordingly, studies concerning nitration of the previously mentioned heterocycles (Figure 1) often make use of both reagents for purposes of comparison. The obtained results are presented in Table 2.

As previously pointed out, nitration of **1a** or **1b** by TNM requires irradiation of the reaction mixture in order to obtain meaningful yields of 2-nitropyridine, while N_2O_4 nitration occurs with similar yields when performed in the dark (entries 1−6).

Curiously, nitration of compounds **2a** and **2b** under similar experimental conditions occurs only at trace levels, and nitration of **3a** or **3b** was ineffective with either TNM or N_2O_4.

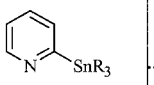
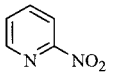
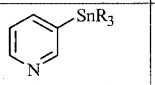
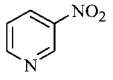
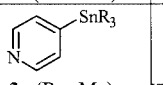
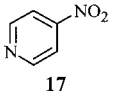
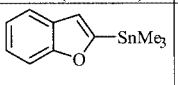
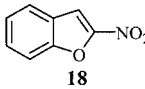
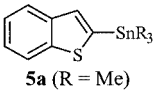
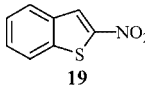
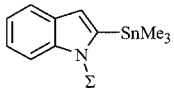
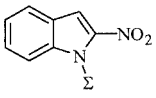
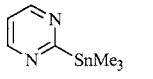
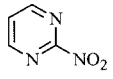
In the case of benzo[*b*]furan or benzo[*b*]thiophene derivatives **4a** and **5a/b**, nitration by TNM is much easier and does not require light in order to take place.

The case of 2-stannylindole derivatives **6a** and **7a** constitutes an intermediate situation in which the reaction, possible even in the absence of light, appears to be significantly improved under moderate irradiation.

Finally, 2-(trimethylstannyl)pyrimidine (**8a**) appears unreactive in attempted nitration by TNM under irradiation or upon treatment by N_2O_4. Similarly, when the reactions of mixtures containing **10**−**14** were subjected to these nitration conditions, no nitro derivatives of the title compounds were detected by GC-MS analysis (in CI^- mode).

For preparative purposes, this nitration method appears to be efficient for the benzo[*b*]furan series, as described previously,[41] and for the benzo[*b*]thiophene series. While the synthesis of 2-nitropyridine seems hard to improve, the use either of more powerful irradiation or of N_2O_4 might increase the yields in the nitroindole series. It is interesting to note that when preliminary experiments related to this work were carried out,[53] while 3-nitroindoles were easily obtainable,[61] the synthesis of 2-nitroindoles was a poorly explored area. Initially, the five-membered ring was constructed from an ortho azido β-nitrostyrene[62] and only

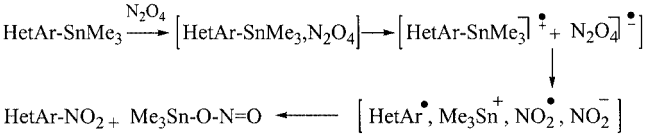
Table 2. Nitration of heteroaryltins with TNM and N_2O_4

Heteroaryltins	N°	Experimental Conditions [a]	Nitroheterocycles[b]	Yield
 **1a** (R = Me) **1b** (R = *n*Bu)	**1a**	TNM,C	 **15**	14%
		TNM, D[d]		43%
		N_2O_4, E[d]		44%
	1b	TNM, A		2%[c]
		TNM, D		15%
		N_2O_4, E		22%
 **2a** (R = Me), **2b** (R = *n*Bu)	**2a**	TNM, D	 **16**	2%
		N_2O_4, E		2%
	2b	TNM, D		<1%
 **3a** (R = Me) **3b** (R = *n*Bu)	**3a**	TNM, D	 **17**	0%
		N_2O_4, E		0%
	3b	TNM, D		0%
 **4a**	**4a**	TNM, A	 **18**	86%
		TNM, B		84%
 **5a** (R = Me) **5b** (R = *n*Bu)	**5a**	TNM, A	 **19**	70%
		TNM, B		73%
	5b	TNM, A		10%[c]
 **6a** (Σ = Me) **7a** (Σ = Boc)	**6a**	TNM, A	 **20** (Σ = Me) **21** (Σ = Boc)	36%[c]
		TNM, B		41%[c]
	7a	TNM, A		30%[c]
		TNM, B		48%[c]
 **8a**	**8a**	TNM, D	 **22**	0%
		N_2O_4, E		0%

[a] Experimental conditions: ***A***: organotin precursor (2 mmol), TNM (1.1 equiv.), DMSO (4 mL), 3 h. ***B***: organotin precursor (2 mmol), TNM (1.1 equiv.), DMSO/CCl_4 (2:3−4 mL), sun-lamp (100 W), 3 h. ***C***: organotin precursor (2 mmol), TNM (2 equiv.), DMSO/CCl_4 (2:3−4 mL), sun lamp (150 W) + AgCl filter, 1 h. ***D***: organotin precursor (2 mmol), TNM (2 equiv.), DMSO/CCl_4 (2:3−4 mL), sun-lamp (1000 W), + AgCl filter, 1 h. ***E***: organotin precursor (2 mmol), N_2O_4 (2 equiv.), DMSO/CCl_4 (2:3−4 mL), dark room temperature, 16 h. For ***B***, ***C*** and ***D*** the analysis of the nitro derivatives was carried out 5 h after the beginning of the reaction. The boiling point of CCl_4 prevents uncontrolled reactions in these experiments. [b] Compounds **15**−**21** were fully identified by comparison with authentic samples or on the basis of their physicochemical characterizations (cf. Exp. Sect.). [c] Pyridine, benzo[*b*]thiophene or *N*-substituted indoles (substitution of SnR_3 by H) were also observed in these cases in 3 to 20% yield, the higher yield of protodestannylation product being obtained from **5b**. [d] Under these experimental conditions, **1a** was almost completely consumed (>95%) to give a mixture of trimethyltin derivatives containing trimethylstannyl nitrite on the basis of the MS spectra (m/z = 211 for ^{120}Sn in EI mode and m/z = 212 for ^{120}Sn in CI mode using NH_3 as reacting gas).

very recently was a synthesis proposed for *N*-Boc and *N*-(arylsulfonyl)indoles in which the nitro derivatives were obtained through the reaction between N_2O_4 and the corresponding 2-lithioindoles.[63] However, this type of trapping of heteroarylanions with N_2O_4 requires the use of frozen reaction mixtures at −120 °C.[63,64] In spite of their higher toxicity, the use of heteroaryltrimethyltins is much more suitable than that of heteroaryltributyltins for preparative purposes, as exemplified by comparison between **1a** and **1b** or between **5a** and **5b**. In this last case, the presence of a high rate for benzo[*b*]thiophene can be explained by abstraction of a β-hydrogen from the *n*-butyl substituents by the heteroaryl radical,[65] consistently with a reaction mechanism involving the fragmentation of an heteroaryltin radical cation as described previously for 2-stannylpyridines (Scheme 3).

For nitration reactions performed with dinitrogen tetroxide, the mechanism of the reaction is likely to be broadly the same but without the requirement for irradiation, thanks to the very easy dissociation of N_2O_4 into nitro radicals above room temperature.[60,61] For compound **1a**, the irradiation reaction without control of the temperature afforded **15** in 22% yield only, probably due to the partial evaporation of N_2O_4. Interestingly, when the reaction flask was placed in a cold nitrogen flow (about 0 °C), the yield of **15** was increased to 37%, corroborating this assumption. Furthermore, we were unable to detect 2-nitrosopyridine in these reactions. This result is in agreement with a prevailing homolytic pathway involving nitro radicals in contrast to the nitration of 1,3-bis(trimethylplumbyl)-2,4,6,8-tetranitrocubane with N_2O_4 in dichloromethane, which affords a mixture of nitro and nitroso derivatives when performed at −15 °C and can be interpreted in terms of the existence of two competitive pathways: a homolytic pathway and an anionic pathway.[52] Accordingly, the obtained results can be reasonably explained as described in Scheme 4 or by a direct homolytic pathway.



Scheme 4. Nitration of heteroaryltrimethyltins by N_2O_4

II.2 Interpretation of the Obtained Results, and Scope and Limitations of the Method

Whatever the nature of the nitration reagent, the key process for obtaining the desired reaction seems to be the ability of the heteroaryltin to give a heteroaryltin radical cation, allowing further fragmentation into heteroaryl radical and triorganotin cation[66−69] as depicted in Schemes 3 and 4. This means that the sequence for the reactivity of heteroaryltins should correlate with the value of the first ionization potential of these organotin precursors.

This value can be broadly determined from theoretical calculations: evaluation of the energy level of the HOMO orbital is convenient for this purpose, since the first ionization potential can be regarded as a shift of an electron from the HOMO to infinity.

In this work, Kohn−Shan orbitals, which are increasingly used to explained chemical properties,[70] have been employed. Indeed, despite systematic errors, their energies turn out to correlate fairly well with associated experimental properties such as bandgaps.[71] The orbitals were calculated at the BP/DN** level (i.e., by use of the Becke−Perdew functional and the DN** basis set).[72] The values of HOMO and LUMO for compounds **1**−**9** and other meaningful compounds are reported in Figure 2. Despite the approximations contained in the calculation methods, the similarity of the molecules allows meaningful comparison between their first ionization potentials.

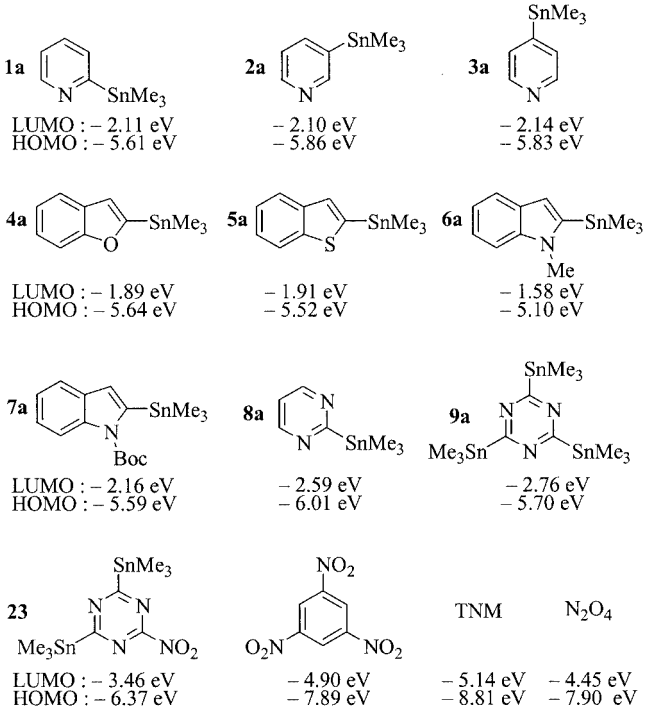


Figure 2. Evaluation of the energies of HOMO and LUMO orbitals

In view of these calculations and the experimental results, it appears that reactivity was obtained only when the HOMO energy of the heteroaryltin was above −5.7/−5.8 eV. With HOMO energy values in the −5.10 to −5.64 eV range, compounds **4a**, **5a**, **6a** and **7a** are the best candidates with which to obtain the primary single electron transfer and subsequent reaction. For π-deficient azaaromatics we are on the borderline, and while reactions were observed in the less disfavourable case of **1a** (HOMO = −5.61 eV), the energy gap with other heteroaryltins seems to be too high to allow significant electron transfer. Accordingly the very low yield obtained with **2a** and the absence of nitration products for **3a** and **8a** are consistent with the above calculations. For comparison, the HOMO energy levels determined by similar calculations are above −5.5 eV for Corey's vinyltins and Einhorn's benzofuryltins. Because of the small differences in evaluated HOMO energies, this good agreement between calculations and experimental results was not really expected; however, we believe that the similarities in the structures of the molecules are responsible for this good fitting. The errors undoubtedly contained in these calculations are of the same type for the series of heteroaryltrimethyltins, allowing comparison between these substrates.

With regard to the nitration of **9a** (had we been if we have been able to obtain this precursor) mononitration might eventually be possible, but further nitration should be prohibited due to the level of the HOMO orbital in the mononitrated compound **23** (HOMO = −6.37 eV). Accordingly, the synthesis of 2,4,6-trinitro-1,3,5-triazine by this nitration method clearly appears to be impossible. In view of the inhibition of TNM nitration of heteroaryltins produced by trinitrobenzene, in spite of a slightly favourable LUMO energy value for TNM (E_{LUMO} = −5.14 eV against −4.90 eV for trinitrobenzene) the higher electronic delocalization in the trinitrobenzene radical anion (due to its flatness) might counterbalance this slight difference in energy. For N_2O_4, the higher LUMO value should be less favourable for single-electron transfer (even though the dissociation of dinitrogen tetroxide radical anion would be expected to be extremely easy), and in this case, the nitration reaction might be due to a purely free radical pathway. In both cases, however, the validity of the comparisons should be regarded with caution due to the fact that calculations have now been performed on completely different molecules.

Conclusion

The above results demonstrate that the nitration of heteroaryltrimethyltins through the use of TNM or N_2O_4 is possible when the HOMO energy level of the organotin is high enough to obtain the heteroaryltrimethyltin radical cation more readily. When the charge-transfer complex is formed, its irradiation facilitates the monoelectronic transfer and the subsequent steps of the reaction, allowing access to nitration products. While unsatisfactorily general, this method constitutes a valuable tool to obtain 2-nitrobenzo[*b*]furans, 2-nitrobenzo[*b*]thiophenes and 2-nitroindoles (with possible improvements in the last case). In contrast, it appears to be incompatible with the nitration of six-membered polyazaheterocycles, due to the low energy levels of the HOMOs of the corresponding heteroaryltrimethytins.

Experimental Section

General Remarks

1. General Starting Materials and Reference Products: ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR spectra were recorded in $CDCl_3$ with Bruker AC 200, Bruker MSL 300 or Bruker AC 400 spectrometers. Chemical shifts are given as δ values relative to tetramethylsilane (^{1}H or ^{13}C) or to tetramethyltin (^{119}Sn). Mass spectra were obtained in EI mode (70 eV) or in CI mode (with CH_4 or NH_3 as reacting gas) on a Thermoquest TSQ 70 or a Hewlett−Packard Engine 5989 A apparatus. The MS analyses were done in direct introduction mode or in GC-MS mode, on either a Varian 3400 or

a HP 5890 chromatograph, respectively, fitted with a 30m × 0.25 mm capillary column (DB-5, MDN-12 or SPB-5). The last column was also used for simple analyses with a FID detector (carrier gas helium). For organotin derivatives, MS spectra are given for ^{120}Sn. TLC separations were performed on Kieselgel 60 F_{254} and preparative chromatography on silica gel 60−230 mesh or 230−400 mesh (for flash chromatography). IR spectra were recorded on Bruker IFS 55 or IFS 110 apparatus and UV/visible spectra on a Perkin−Elmer-Lambda 19.

Alkyllithium reagents (*n*BuLi, *s*BuLi, *t*BuLi) are Chemetall products, while organotin or organosilicon starting materials (Bu_3SnCl, Me_3SnCl, Bu_3SnH, Me_6Sn_2, Me_3SiCl) are commercially available compounds. THF, Et_2O and DME were used after distillation over sodium/benzophenone, and reactions involving organolithium reagents were performed under dry argon. Pyridine, 2-bromopyridine, 3-bromopyridine, 2-chloropyrimidine, 2-bromopyrimidine and cyanuryl chloride are commercially available compounds, as are benzo[*b*]furan, benzo[*b*]thiophene and indole. 4-Bromopyridine (available as hydrochloride) was obtained after NaOH treatment, *N*-methylindole[73] and *N*-(*tert*-butoxycarbonyl)indole[74] were obtained by previously described procedures, and the trimerization of cyanogen bromide[75] was used to obtain cyanuryl bromide [^{13}C NMR (DMSO): δ = 150.0. MS: *m*/*z* = 321/319/317/315 (100), 236/238/240 (98), 131/133 (79), 79/81 (14)].

The syntheses of authentic samples of 2-nitropyridine[76] and 3-nitropyridine[77,78] were achieved from the corresponding aminopyridines by the literature methods and those of 4-nitropyridine by nitration of pyridine *N*-oxide, followed by reduction of the obtained 4-nitropyridine *N*-oxide.[79,80]

Characterization of 15, 16 and 17

2-Nitropyridine (15): ^1H NMR ([D$_6$]DMSO): δ = 7.90 (ddd, *J* = 7.0, 4.7, 1.5 Hz, 1 H, H^5), 8.25 (ddd, *J* = 7.6, 7.0, 1.7 Hz, 1 H, H^4), 8.32 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 1 H, H^3), 8.69 (ddd, *J* = 4.7, 1.7, 1.0 Hz, 1 H, H^6) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 118.2, 130.0, 140.9, 149.0, 156.5 ppm. MS (EI): *m*/*z* = 124 (7), 94 (12), 78 (100), 66 (7), 52 (10), 51 (38). IR: ṽ = 3090, 1563, 1537, 1431, 1356, 1041, 996, 742, 705 cm^{-1}.

3-Nitropyridine (16): ^1H NMR (CD_2Cl_2): δ = 7.54 (ddd, *J* = 8.4, 4.8, 0.6 Hz, 1 H, H^5), 8.48 (ddd, *J* = 8.4, 2.6, 1.5 Hz, 1 H, H^4), 8.91 (dd, *J* = 4.8, 1.5 Hz, 1 H, H^6), 9.42 (dd, *J* = 2.6, 0.6 Hz, 1 H, H^2) ppm. ^{13}C NMR (CD_2Cl_2): δ = 124.3, 131.4, 144.8, 145.3, 155.2 ppm. MS (EI): *m*/*z* = 124 (100), 108 (2), 78 (26), 51 (26). IR: ṽ = 3094, 1603, 1573, 1528, 1482, 1427, 1355, 1195, 727, 693 cm^{-1}.

4-Nitropyridine (17): ^1H NMR ([D$_6$]DMSO): δ = 8.13 (dd, *J* = 4.6, 1.6 Hz, 2 H, H^2 and H^6), 8.98 (dd, *J* = 4.6, 1.6 Hz, 2 H, H^3 and H^5) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 116.3, 152.2, 153.5 ppm. MS (EI): *m*/*z* = 124 (100), 78 (93), 51 (87), 46 (3). IR: ṽ = 3123, 3046, 1612, 1573, 1540, 1480, 1403, 1357, 1224, 995, 847 cm^{-1}.

2. Synthesis of Silylated and Stannylated Heteroaryltins

2.1. Preparation of Silyl and Stannylpyridines: A solution of bromopyridine (15 mmol) in dry THF (30 mL) was placed in a Schlenk tube under an inert atmosphere (argon). After the mixture had been cooled to −95 °C, a *t*BuLi solution (1.7 M in pentane, 10 mL) was added dropwise and the reaction mixture was stirred for 45 min before quenching with triorganotin chloride or chlorotrimethylsilane (1.1 equiv.). After further stirring for 45 min at −90 °C, the reaction mixture was allowed to warm up to −40 °C before hydrolysis (H_2O, 20 mL). The aqueous phase was extracted with Et_2O (3 × 20 mL) before washing with an aqueous NaCl solution and drying on $MgSO_4$. After evaporation of the solvent, the crude residue was purified by distillation (**1a**, **1c**, **2a**, **2c**), by liquid chromatography (hexane/EtOAc, 80:20) for **1b**, **2b** and **3b**, or by crystallization from diethyl ether for **3a**.

In these preparations of already known products,[28−31,81] we have chosen the isolation of products of high purity though in yields lower than already published in the literature.

2-(Trimethylstannyl)pyridine (1a): 2 g, 55% yield, bp_{13} = 80 °C. ^1H NMR ([D$_6$]DMSO): δ = 0.26 (s, 9 H, J_{Sn-H} = 54/56 Hz, $(CH_3)_3$], 7.22 (ddd, *J* = 7.4, 4.8, 1.4 Hz, 1 H, H^5), 7.51 (dd, *J* = 7.4, 1.4 Hz, 1 H and J_{Sn-H} = 34 Hz, H^3), 7.60 (td, *J* = 7.4, 1.4 Hz, 1 H, H^4), 8.67 (dd, *J* = 4.8, 1.4 Hz, 1 H, H^6) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = −9.2 (J_{Sn-C} = 331/346 Hz), 122.5 (J_{Sn-C} = 12 Hz), 131.6 (J_{Sn-C} = 88/92 Hz), 133.75 (J_{Sn-C} = 35 Hz), 150.6 (J_{Sn-C} = 68 Hz), 172.9 (J_{Sn-C} = 563/589 Hz) ppm. ^{119}Sn NMR ([D$_6$]DMSO): δ = −48.8 ppm. MS (EI): *m*/*z* = 243 (29), 228 (100), 198 (47), 165 (7), 135 (36), 120 (7), 93 (4), 78 (2), 51 (2). IR: ṽ = 3059, 2978, 2914, 1568, 1555, 1449, 1415, 1187, 771, 750, 712 cm^{-1}.

2-(Tributylstannyl)pyridine (1b): 4.04 g, 73% yield. ^1H NMR ($CDCl_3$): δ = 0.85−1.70 [m, 27 H, (*n*Bu)$_3$], 7.07 (ddd, *J* = 7.4, 4.9, 1.7 Hz, 1 H, and J_{SnH} = 8 Hz, H^5), 7.38 (ddd, *J* = 7.4, 1.7, 1.0 Hz, 1 H, and J_{Sn-H} = 17 Hz, H^3), 7.46 (td, *J* = 7.4, 1.7 Hz, 1 H and J_{Sn-H} = 14 Hz, H^4), 8.71 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1 H, H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.7 (J_{Sn-C} = 323/338 Hz), 13.6, 26.8 (J_{Sn-C} = 56 Hz), 29.1 (J_{Sn-C} = 20 Hz), 122.6 (J_{Sn-C} = 10 Hz), 133.1 (J_{Sn-C} = 76 Hz), 134.0 (J_{Sn-C} = 31 Hz), 151.3 (J_{Sn-C} = 58 Hz), 175 (J_{Sn-C} = 474/496 Hz) ppm. MS (CI$^+$/CH_4): *m*/*z* = 398 (5), 370 (30), 312 (100), 291 (5), 256 (15), 235 (3), 198 (25), 177 (2), 121 (2), 80 (5), 57 (4). IR: ṽ = 3059, 2957, 2925, 2870, 2850, 1567, 1555, 1448, 1376, 747, 598, 512 cm^{-1}.

3-(Trimethylstannyl)pyridine (2a): 1.28 g, 35% yield, bp_{13} = 75 °C. ^1H NMR ([D$_6$]DMSO): δ = 0.28 (s, 9 H, J_{Sn-H} = 55/57 Hz, $(CH_3)_3$], 7.28 (ddd, *J* = 7.3, 4.8, 0.9 Hz, 1 H and J_{Sn-H} = 18 Hz, H^5), 7.82 (dt, *J* = 7.3, 1.7 Hz, 1 H and J_{Sn-H} = 41 Hz, H^4), 8.47 (dd, *J* = 4.8, 1.7 Hz, 1 H and J_{Sn-H} = 8 Hz, H^6), 8.58 (dd, *J* = 1.7, 0.9 Hz, 1 H and J_{Sn-H} = 23 Hz, H^2) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = −9.3 (J_{Sn-C} = 341/357 Hz), 123.9 (J_{Sn-C} = 32 Hz), 137.1 (J_{Sn-C} = 384/402 Hz), 143.4 (J_{Sn-C} = 29 Hz), 149.1 (J_{Sn-C} = 8 Hz), 155.2 (J_{Sn-C} = 41 Hz) ppm. MS (EI): *m*/*z* = 243(23), 228(100), 213 (12), 198 (29), 165 (6), 145 (5), 135 (14), 120 (7), 78 (8), 51 (8). IR: ṽ = 3065, 2981, 2915, 1563, 1467, 1394, 1192, 1030, 774 cm^{-1}.

3-(Tributylstannyl)pyridine (2b): 3.21 g, 58% yield. ^1H NMR (CD_2Cl_2): δ = 0.85−1.60 [m, 27 H, (*n*Bu)$_3$], 7.22 (ddd, *J* = 7.3, 4.8, 0.9 Hz, 1 H, H^5), 7.76 (dt, *J* = 7.3, 1.8 Hz, 1 H and J_{Sn-H} = 35 Hz, H^4), 8.46 (dd, *J* = 4.8, 1.8 Hz, 1 H, H^6), 8.58 (dd, *J* = 1.8, 0.9 Hz, 1 H, H^2) ppm. ^{13}C NMR (CD_2Cl_2): δ = 9.8 (J_{Sn-C} = 336/344 Hz), 13.8, 27.7 (J_{Sn-C} = 57 Hz), 29.3 (J_{Sn-C} = 20 Hz), 124.9 (J_{Sn-C} = 28 Hz), 138.2 (J_{Sn-C} = 330/337 Hz), 145.3 (J_{Sn-C} = 23 Hz), 150.4 (J_{Sn-C} = 7 Hz), 157.4 (J_{Sn-C} = 33 Hz) ppm. MS (CI$^+$/CH_4): *m*/*z* = 398 (17), 370 (75), 312 (100), 291 (15), 256 (12), 235 (3), 198 (9), 177 (1), 80 (7), 57 (6). IR: ṽ = 3056, 2958, 2926, 2870, 2853, 1561, 1460, 1391, 787 cm^{-1}.

4-(Trimethylstannyl)pyridine (3a): 0.19 g, 5% yield. ^1H NMR ($CDCl_3$): δ = 0.22 (s, 9 H, J_{Sn-H} = 54/56 Hz, $(CH_3)_3$], 7.50 (m, 2 H, J_{Sn-H} = 39 Hz, H^3 and H^5), 8.47 (m, 2 H, J_{Sn-H} = 12 Hz, H^2 and H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = −9.6 (J_{Sn-C} = 345/362 Hz), 131.8 (J_{Sn-C} = 27 Hz), 146.5 (J_{Sn-C} = 33 Hz), 152.2 ppm. MS (EI): *m*/*z* = 243 (26), 228 (100), 198 (29), 165 (10), 135 (22), 120

(18), 78 (2), 51 (6). IR: $\tilde{\nu}$ = 3063, 3034, 2989, 2915, 1590, 1527, 1409, 1225, 119, 804, 782 cm^{-1}.

4-(Tributylstannyl)pyridine (3b): 1.38 g, 25% yield. ^1H NMR (CD_2Cl_2): δ = 0.85−1.56 [m, 27 H, ($nBu)_3$], 7.38 (m, 2 H, J_{Sn-H} = 36 Hz, H^3 and H^5), 8.44 (m, 2 H, J_{Sn-H} = 7 Hz, H^2 and H^6) ppm. ^{13}C NMR (CD_2Cl_2): δ = 9.8 (J_{Sn-C} = 328/343 Hz), 13.8, 27.7 (J_{Sn-C} = 55/57 Hz), 29.3 (J_{Sn-C} = 20 Hz), 132.3 (J_{Sn-C} = 22 Hz), 148.6 (J_{Sn-C} = 29 Hz), 153.3 (J_{Sn-C} = 311/326 Hz) ppm. MS (EI): *m*/*z* = 369 (10), 312 (82), 256 (82), 198 (100), 145 (4), 121 (10), 80 (6), 57 (2), 41 (5). IR: $\tilde{\nu}$ = 3046, 2956, 2927, 2871, 2853, 1570, 1464, 1399, 1377, 1095, 790, 650, 465 cm^{-1}.

2.2. Preparation of 2-Stannylated Benzo[*b*]furans, Benzo[*b*]thiophenes and Indoles

2-(Trimethylstannyl)benzo[*b*]furan (4a):[42,82] A stirred solution of benzo[*b*]furan (16 mmol) in diethyl ether (16 mL) was cooled to −78 °C before dropwise addition of a solution of *n*BuLi in hexanes (1.1 equiv.). The reaction temperature was allowed to warm to −10 °C over 2 h before dropwise addition of trimethyltin chloride (1.92 mmol, 1.2 equiv.). After further stirring for 16 h, hydrolysis was achieved at 0 °C with water (20 mL) and the reaction mixture was extracted with diethyl ether (3 × 20 mL). After drying of the organic layer on $MgSO_4$ and usual workup treatment, **4a** was distilled as a colourless oil ($bp_{0.05}$ = 91 °C, 3.34 g, 78% yield). ^1H NMR ($CDCl_3$): δ = 0.38 (s, 9 H, J_{Sn-H} = 55/58 Hz, $(CH_3)_3$], 6.90 (br. d, 1 H, J_{Sn-H} = 9 Hz), 7.1−7.3 (m, 2 H) 7.4−7.6 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = −9.2 (J_{Sn-C} = 358/373 Hz), 111.2, 117.8 (J_{Sn-C} = 63 Hz), 120.7, 122.4, 123.9, 128.2, 158.8, 165.2 ppm. MS (EI): *m*/*z* = 282 (28), 267 (91), 237 (68), 209 (14), 132 (40), 131 (100), 120 (26), 117 (20), 89 (93), 63 (6).

2-Triorganostannylbenzo[*b*]thiophenes:[43] The preparation of these compounds was achieved as for **4a**, but with THF in place of diethyl ether as solvent and a higher dilution (8 mmol in 16 mL THF). At the end of the reaction, the crude compounds were purified on silica gel (eluent: hexanes)

2-(Trimethylstannyl)benzo[*b*]thiophene (5a): 1.96 g, 82% yield. ^1H NMR ($CDCl_3$): δ = 0.42 (s, 9 H, J_{Sn-H} = 55/58 Hz, $(CH_3)_3$], 7.27 and 7.32(2td, 2 H, *J* = 7.4, 1.5 Hz, H^5 and H^6), 7.41 (br. d, 1 H, *J* = 1 Hz and J_{Sn-H} = 25 Hz, H^3), 7.75−7.90 (m, 2 H, H^4 and H^7) ppm. ^{13}C NMR ($CDCl_3$): δ = −8.4 (J_{Sn-C} = 356/372 Hz), 121.9 (J_{Sn-C} = 5 Hz), 122.8, 123.5, 123.8 (J_{Sn-C} = 3.5 Hz), 131.9 (J_{Sn-C} = 28 Hz), 140.3 (J_{Sn-C} = 352/369 Hz), 141.0 (J_{Sn-C} = 45 Hz), 144.2 (J_{Sn-C} = 19 Hz) ppm. MS (EI): *m*/*z* = 298 (22), 283 (100), 253 (59), 133 (9), 101 (30).

2-(Tributylstannyl)benzo[*b*]thiophene (5b): 2.92 g, 86% yield. ^1H NMR ($CDCl_3$): δ = 0.80−1.70 [m, 27 H, ($nBu)_3$], 7.41 and 7.48 (2dt, 2 H, *J* = 7, 1.4 Hz, H^5 and H^6), 7.58 (d, *J* = 0.75 Hz, 1 H and J_{Sn-H} = 25 Hz, H^3), 7.95 to 8.08 (m, 2 H, H^4 and H^7) ppm. ^{13}C NMR ($CDCl_3$): δ = −10.9 (J_{Sn-C} = 340/355 Hz), 13.7, 27.3 (J_{Sn-C} = 58 Hz), 29.0 (J_{Sn-C} = 21 Hz), 121.8 (J_{Sn-C} = 4 Hz), 122.7, 123.3, 123.7 (J_{Sn-C} = 3 Hz), 132.1 (J_{Sn-C} = 23 Hz), 139.7 (J_{Sn-C} = 285/271 Hz), 141.1 (J_{Sn-C} = 39 Hz), 144.4 (J_{Sn-C} = 14 Hz).

2-(Trimethylstannyl)indoles (6a, 7a):[44] In these series, the preparations of **6a** and **7a** were achieved by procedures already described for tributylstannyl analogues,[44] starting from 1-methylindole (3 g) or 1-Boc-indole (2 g).

1-Methyl-2-(trimethylstannyl)indole (6a): $bp_{0.07}$ = 105 °C, 5.27 g, 78% yield. ^1H NMR ($CDCl_3$): δ = 0.41 (s, 9 H, J_{Sn-H} = 54/57 Hz, $(CH_3)_3$], 3.81 (s, 3 H, CH_3), 6.61 (d, *J* = 0.9 Hz, 1 H J_{Sn-H} = 16 Hz, H^3), 7.0 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 1 H, H^5), 7.18 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1 H, H^6), 7.31 (dd, *J* = 8.1, 1.2 Hz, 1 H, H^7), 7.58 (ddd, *J* = 7.8, 1.4, 0.9 Hz, 1 H, H^4) ppm. The assignment of the protons was performed on the basis of $^nJ_{H,H}$ and NOE effect between N−Me and H^7. ^{13}C NMR ($CDCl_3$): δ = −8.7 (J_{Sn-C} = 354/371 Hz), 33.9, 108.8, 111.1 (J_{Sn-C} = 50 Hz), 118.8, 119.9, 121.2, 128.8 (J_{Sn-C} = 44 Hz), 139.6 (J_{Sn-C} = 24 Hz), 142.3 (J_{Sn-C} = 429/450 Hz).

1-(*tert*-Butoxycarbonyl)-2-(trimethylstannyl)indole (7a): Colourless crystals obtained after flash chromatography with hexanes/EtOAc, 95:5, as eluent, 2.74 g, 78% yield: ^1H NMR ($CDCl_3$): δ = 0.45 (s, 9 H, J_{Sn-H} = 55/58 Hz, $(CH_3)_3$], 1.83 [s, 9 H, $(CH_3)_3$], 6.87 (d, *J* = 0.7 Hz, 1 H and J_{Sn-H} = 19 Hz, H^3), 7.31 (dt, *J* = 7.2, 1.4 Hz, 1 H, H^5), 7.35 (dt, *J* = 7.2, 1.7 Hz, 1 H, H^6), 7.60−7.70 (m, 1 H, H^7), 8.06−8.12 (m, 1 H, H^4) ppm. ^{13}C NMR ($CDCl_3$): δ = −7.2 (J_{Sn-C} = 372/392 Hz), 28.1, 83.9, 115.2, 118.1 (J_{Sn-C} = 45 Hz), 120.1, 122.3, 123.5, 132.1, 137.3, 143.1, 152.1.

2.3. Preparation of 2-(Triorganostannyl)pyrimidines 8a and 8b

These compounds were obtained by use of stannyl anions according to Undheim.[33] (Tributylstannyl)lithium was obtained from tributyltin hydride[83] and (trimethylstannyl)sodium from trimethyltin chloride.[84]

2-(Tributylstannyl)pyrimidine (8b): Diisopropylamine (1.38 mL) in dry THF (10 mL) was placed in a Schlenk tube before cooling at −10 °C and further dropwise addition of *n*BuLi solution (6.17 mL, 9.87 mmol). After 5 min stirring, tributyltin hydride (2.65 mL, 9.88 mmol) in THF (10 mL) was added at 0 °C and the mixture was stirred for 20 min before cooling at −78 °C. A solution of 2-chloropyrimidine (1.13 g, 9.88 mmol) in THF (10 mL) was added dropwise at −78 °C whilst stirring. After 1 h, the reaction mixture was allowed to warm up at 0 °C and hydrolysis was achieved with a saturated aqueous solution of NH_4Cl. Subsequent treatments (Et_2O extraction, drying on $MgSO_4$, concentration and flash chromatography) afforded compound **8b** (2.23 g, 61% yield) as a colourless oil. ^1H NMR ($CDCl_3$): δ = 0.83−1.63 [m, 27 H, ($nBu)_3$], 7.11 (t, *J* = 5.0 Hz, 1 H, H^5), 8.67 (d, *J* = 5 Hz, 2 H, H^4 and H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.2 (J_{Sn-C} = 326/341 Hz), 13.7, 27.2 (J_{Sn-C} = 56 Hz), 28.9 (J_{Sn-C} = 21 Hz), 119.3 (J_{Sn-C} = 9 Hz), 154.7 (J_{Sn-C} = 41 Hz, 2C), 189.1 ppm. MS (EI): *m*/*z* = MS (EI): *m*/*z* = 314 (6), 313 (18), 257 (24), 255 (38), 201 (17), 199 (25), 177 (8), 174 (8), 121 (15), 81 (100). MS (CI, NH_3): *m*/*z* = 371 (100), 81 (11). IR: $\tilde{\nu}$ = 3018, 2956, 2927, 2871, 2853, 1552, 1544, 1378, 983, 960, 627, 600, 509 cm^{-1}.

2-(Trimethylstannyl)pyrimidine (8a): In this case, on a 10 mmol scale, poor yields were obtained with (trimethylstannyl)lithium in THF while a moderate (27%) yield of **8a** (0.66 g) was obtained (after flash chromatography) with (trimethylstannyl)sodium in DME as reagent at 0 °C. Attempted cross couplings between 2-chloropyrimidine or 2-bromopyrimidine (3 mmol) and hexamethylditin (3 equiv.) in the presence of $Pd(PPh_3)_4$ (1.5%) were achieved in degassed DMF (10 mL) upon warming at 150 °C for 15 h. The best results were obtained with 2-chloropyrimidine, but in spite of a conversion rate over 50%, **8a** was never isolated in yields above 20%, due to subsequent Stille cross coupling. ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9 H, J_{Sn-H} = 55 Hz, $(CH_3)_3$], 6.75 (t, *J* = 5 Hz, 1 H, H^5), 8.29 (d, *J* = 5 Hz, 2 H, H^4 and H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = −9.4 (3C), 119.4, 154.7 (2C), 188.7 ppm. MS (EI): *m*/*z* = 244 (14), 229 (45), 165 (25), 135 (24), 79 (100), 52 (45).

2.4. Attempts to Prepare 9a and 9b

In attempts to obtain **9b**, stannylation was performed with an excess of (tributylstannyl)lithium (prepared as described previously for **8a**), which was treated with heteroarylhalide (cyanuryl chloride or 2,4-dichloro-6-phenoxy-1,3,5-triazine). Compound **9b** was never detected in the MS (either in direct introduction mode or in GC-MS mode): in GC-MS mode, fragmentation patterns for one peak might be indicative of the presence of tributyltin cyanide [*m*/*z* = 317 (5); 260 (100); 204 (25); 148 (8); 146 (10); 121 (7)].

In an attempt to obtain **9a**, a benzene solution (6 mL) of cyanuryl bromide[75] (1 mmol, 0.32 g) was warmed with hexamethylditin (2 g) in the presence of $Pd[P(Ph)_3]_4$ (57 mg) at 150 °C for 15 h in a sealed tube.

GC-MS analysis of the reaction mixture allowed detection of compounds with fragmentation patterns compatible with **10**−**14** among other organotin compounds, but without **9a**.

10: *m*/*z* = 245 (15); 230 (36); 203 (17); 176 (99); 165 (100); 146 (40); 135 (42).

11: *m*/*z* = 259 (5); 244 (78); 217 (8); 203 (7); 176 (100); 165 (68); 146 (30); 135 (26).

12: *m*/*z* = 273 (2); 258 (100); 217 (18); 176 (97); 165 (48); 146 (27); 135 (2).

13: *m*/*z* = 421 ($^{120}Sn + {}^{118}Sn$, 3); 406 ($^{120}Sn + {}^{118}Sn$,10); 354 ($^{120}Sn + {}^{118}Sn$, 44); 258 (5); 232 (6); 176 (18); 165 (100); 146 (9); 135 (15).

14: *m*/*z* = 432 ($^{120}Sn + {}^{118}Sn$, 4); 417 ($^{120}Sn + {}^{118}Sn$, 3); 354 ($^{120}Sn + {}^{118}Sn$, 20); 176 (9); 165 (100); 149 (10); 135 (17).

3. Nitration of Heteroaryltins

3.1. Nitrodestannylation of 2-Stannylpyridines by TNM: 2-(Triorganostannyl)pyridine (1.35 mmol) in DMSO (5 mL) was placed under a nitrogen flow in a 50 mL three-necked Pyrex reactor fitted with a reflux condenser, before dropwise addition of TNM (15 mmol). The reaction mixture was allowed to react at the desired temperature for the time mentioned in the theoretical section. After hydrolysis, extraction by chloroform (4×10 mL) and usual workup treatments (drying $MgSO_4$, concentration), the crude compound was examined in GC-MS mode on ions *m*/*z* = 125 (CI^+) or *m*/*z* = 124 (CI^-).

The inhibition experiments were carried out by addition of Irganox (1.6 g) or trinitrobenzene (0.29 g) before TNM addition. When reactions were performed under irradiation, the lamp was placed at 30 cm from the reactor and the AgCl filter (when used) was intercalated at 3 cm from the flask.

Reaction times and characteristics of the lamps are described in the theoretical section. Attempted nitration of **8a** was carried out under similar experimental conditions.

Characterization of the Charge-Transfer Complex between 1a and TNM

When **1a** and TNM are mixed in DMSO, a yellow coloration appears and the UV spectrum exhibits three bands at 290 nm, 350 nm and 425 nm (broad). Similarly, bands at 1356, 1537 and 1547 cm^{-1} in the IR spectrum of **1a** are shifted to 1268, 1611 and 1644 cm^{-1} in the complex **1a**-TNM.

The NMR spectra were also strongly modified:

− The ^{119}Sn NMR signal of **1a** (solvent $[D_6]$DMSO) was shifted to δ = −32.3 ppm after addition of TNM (instead of δ = −48.8 ppm for **1a** alone).

− In the ^1H NMR spectrum, the signals obtained for **1a**-TNM were shifted as indicated below (the values in brackets are those of **1a** in $[D_6]$DMSO).

Me_3Sn: δ = 0.48 ppm (δ = 0.27 ppm); H^6: 8.92 ppm (δ = 8.67 ppm); $H^{3,4,5}$; 7.81−8.40 ppm (7.18−7.61 ppm).

− The ^{13}C NMR spectra were modified similarly:

C^2: δ = 170.2 ppm (against 172.8 for **1a** and 156.5 for **15**).

C^3: δ = 135.1 ppm (against 133.7 for **1a** and 130 for **15**).

C^4: δ = 142.8 ppm (against 131.6 for **1a** and 140.9 for **15**).

C^5: δ = 125.7 ppm (against 122.5 for **1a** and 118.2 for **15**).

C^6: δ = 143 ppm (against 150.6 for **1a** and 149 for **15**).

3.2. Nitrodestannylation of Stannylpyridines and 2-Stannylpyrimidine with N_2O_4

Compound **1a** (1 g, 4.11 mmol), CCl_4 (2.5 mL) and DMSO (2 mL) were placed in a two-necked round-bottomed flask fitted with a reflux condenser and a cold dropping funnel (in order to add N_2O_4 as a liquid). The reaction mixture was placed in an ice bath and N_2O_4 (0.5 mL, 8.22 mmol, $d^{-10°C} = 1.49$) was added dropwise. The reaction mixture was subsequently allowed to warm up to room temperature and stirred in the dark for 16 h. For **1a**, the obtained yield of 2-nitropyridine **15** was 44% (0.22 g). Similar experimental conditions were used for **2a**, **3a** and **8a**. Nitropyridines were unambiguously identified by comparison with authentic samples.

3.3. Nitrodestannylation of Five-Membered Heterocycles. Typical Procedure: 1-Methyl-2-(trimethylstannyl)indole (**6a**, 300 mg, 1.03 mmol) in DMSO (2.5 mL) was placed in a round-bottomed flask before addition of TNM (140 μL; 1.1 equiv.; 1.18 mmol) at room temperature. After 3 h, water (10 mL) and chloroform (5 mL) were added successively. Subsequent extraction with chloroform (3 × 10 mL) afforded an organic phase, which was subjected to usual workup treatments (drying on $MgSO_4$, concentration, flash chromatography) to afford yellow crystals of **20**. When the influence of the light had been studied, a sun-lamp (100 W) was placed at 30 cm from the Pyrex reactor. Similar experimental conditions were used for nitrodestannylation of **4a**, **5a**, **5b** and **7a** with possible scales of 2 mmol of heteroaryltin.

Generally, a unique nitro derivative was obtained in these reactions, except for the nitrodestannylation of **6a**, from which nitroindole **20** was obtained together with a more polar compound, which might be 1-methyl-2,3-dinitroindole or the oxidized parent.

Physicochemical Data of the Obtained Five-Membered Heterocycles

2-Nitrobenzo[*b*]furan (18): Brown solid, 0.34 g, 86% yield. ^1H NMR ($CDCl_3$): δ = 7.42 (ddd, 1 H, *J* = 8, 6.2, 2 Hz, H^5), 7.60 (td, 1 H, *J* = 6.2, 1.2 Hz, H^6), 7.62 (br. d, *J* = 6.2, 2 Hz, 1 H, H^7), 7.66 (d, *J* = 0.6 Hz, 1 H, H^3), 7.77 (ddd, 1 H, *J* = 8, 1.2, 0.6 Hz, H^4) ppm. ^{13}C NMR ($CDCl_3$): δ = 107.2, 112.7, 124.0, 125.3, 125.8, 130.0, 153.0, 153.4 ppm. MS (EI): 163 (51), 147 (5), 133 (100), 105 (57), 89 (87), 77 (61), 63 (89), 62 (36), 51 (43), 50 (25), 46 (7), 39 (48), 37 (18), 30 (33). MS (CI^+/NH_3): *m*/*z* = 198 (26), 181 (100), 134 (37), 133 (20). IR: $\tilde{\nu}$ = 3170−2920, 2360, 2330, 1616, 1563, 1517, 1368, 1245, 1090, 833, 756, 730 cm^{-1}.

It can be seen that the ^1H NMR spectroscopic data are in agreement with those reported in the closely related series of 3-substituted 2-nitrobenzo[*b*]furans.[41]

2-Nitrobenzo[*b*]thiophene (19): Yellow crystals, 0.26 g, 73% yield. MS (EI): *m*/*z* = 179 (83), 149 (30), 133 (33), 121 (49), 93 (9), 89 (100), 77 (17), 69 (14), 63 (23), 50 (11), 46 (8), 45 (15), 39 (12), 30 (28). NMR spectroscopic data for this compound are identical with those reported in the literature.[85]

1-Methyl-2-nitroindole (20): Yellow crystals, 73 mg, 40% yield. ^1H NMR ($CDCl_3$): δ = 4.07 (s, 3 H, CH_3), 7.20 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1 H, H^5), 7.37 (br. d, 1 H, *J* = 8.5 Hz, H^7), 7.47 (ddd, *J* = 8.5, 6.8, 1.2 Hz, 1 H, H^6), 7.50 (br. s, 1 H, H^3), 7.69 (br. dt, *J* = 8.1, 0.9 Hz, 1 H, H^4) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.5, 106.1, 110.8, 122.2, 123.6, 123.8, 127.6, 138.0, 141.8 ppm. MS (EI): *m*/*z* = 176 (91), 175 (4), 159 (50), 146 (27), 129 (33), 102 (1), 91 (17), 89 (100), 77 (11), 63 (15). IR: $\tilde{\nu}$ = 3180−2900, 2360, 2330, 1700, 1653, 1559, 1533, 1506, 1473, 1457, 1380, 1337, 1293, 1235, 746 cm^{-1}.

For this compound, the complete assignment of the NMR spectra was performed on the basis of 2D correlation $^1H/^1H$ and $^1H/^{13}C$ after an unambiguous assignment of H^7 on the basis of a 7% NOE effect with the *N*-methyl group.

1-Methyl-2,3-dinitroindole (or Parent Oxidised Derivative): ^1H NMR ($CDCl_3$): δ = 3.34 (s, 3 H, CH_3), 7.00 (br. d, 1 H, *J* = 8.0 Hz), 7.27 (ddd, *J* = 8.0, 7.8, 0.9 Hz, 1 H), 7.64 (ddd, *J* = 7.8, 7.7, 1.2 Hz, 1 H), 7.68 (ddd, 1 H, *J* = 7.7, 1.2, 0.5 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.6, 110.1, 124.7, 127.0, 135.4, 143.9, 145.6, 153.1, 158.6 ppm. MS (EI): *m*/*z* = 237 (3), 221 (1), 219 (2), 191 (46), 176 (15), 161 (12), 160 (13), 133 (46), 131 (18), 117 (14), 105 (90), 104 (84), 90 (42), 89 (32), 78 (24), 77 (25), 76 (27), 75 (15), 63 (18), 58 (16), 46 (15), 43 (61), 39 (10), 31 (23), 30 (100).

1-*tert*-Boc-2-nitroindole (21): Yellow crystals, 0.25 g, 48% yield. ^1H NMR ($CDCl_3$): δ = 1.60 [s, 9 H, $(CH_3)_3$], 7.35 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1 H, H^6), 7.36 (d, *J* = 0.75 Hz, 1 H, H^3), 7.54 (ddd, 1 H, *J* = 8.5, 7.2, 1 Hz, H^5), 7.68 (ddd, 1 H, *J* = 8, 1, 0.9 Hz, H^7), 8.0 (ddd, *J* = 8.5, 0.9, 0.7 Hz, 1 H, H^4) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.3, 86.1, 110.8, 114.4, 123.1, 124.1, 124.3, 128.9, 136.4, 142.4, 147.4 ppm. MS (EI): *m*/*z* = 262 (3), 189 (3), 162 (80), 145 (9), 132 (20), 115 (13), 57 (100), 41 (31), 30 (5), 29 (16). IR: $\tilde{\nu}$ = 3180−2850, 2360, 2330, 1747, 1544, 1511, 1446, 1382, 1297, 1160, 1132, 1081, 836, 766, 746 cm^{-1}.

Complete assignment of the signals was performed on the basis of decoupling experiments (^1H NMR) and $^1H/^{13}C$ 2D NMR spectra.

It is worth noting that compounds **20** and **21** are identical with those obtained by G.W. Gribble.[63]

4. Theoretical Calculations

All calculations were carried out with the Spartan program Version 5.1.1 running on a SGI workstation, using default values of numerical parameters.[72]

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