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Syntheses of 3-Substituted 2,3-Dihydrobenzofuranes, 1,2-Dihydronaphtho(2,1-*b*)furanes, and 2,3-Dihydro-1*H*-indoles by Tandem Ring Closure−$S_{RN}1$ Reactions

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3-Substituted 2,3-dihydrobenzofuranes (**7a**−**c**), 1,2-dihydronaphtho(2,1-*b*)furanes (**10a**−**c**), and N-substituted 2,3-dihydro-1*H*-indoles (**8a**−**c**, **9a**,**b**) are obtained in very good yields by $S_{RN}1$ photostimulated reactions in liquid ammonia from adequate haloaromatic compounds ortho-substituted with a suitable double bond (**3a**,**b**; **4a**,**b**; **5a**; **6a**,**b**) and Me_3Sn^-, Ph_2P^-, and $^-CH_2NO_2$ anions. The novelty of the work involves the versatile application of a 5-*exo* ring closure process during the propagation cycle of the $S_{RN}1$ reaction; the alkyl radical intermediates formed react with the nucleophiles to afford the ring closure-substituted heterocycles. The factors governing the observed product distribution are discussed.

Introduction

The radical nucleophilic substitution, or $S_{RN}1$ reaction, is a chain process with radicals and radical anions as intermediates, through which an aromatic nucleophilic substitution is obtained. The scope of the process has considerably increased, and nowadays it is an important synthetic possibility to achieve substitution of different substrates.[1] Several nucleophiles can be used such as carbanions and anions from compounds bearing heteroatoms, which react to form new C−C or C−heteroatom bonds in good yields. Many substituents are compatible with the reaction. In general, substituents such as NO_2 groups are not suitable for $S_{RN}1$ substitution on aromatic substrates.[1]

This chain process requires an initiation step. The most frequently used methods for initiation are chemical initiation by alkali metals in liquid ammonia, electrochemical initiation at a cathode, and photoinitiation. Other methods include the use of Fe^{2+}, SmI_2, or Na(Hg). In a few systems, a thermal (spontaneous) initiation is observed. The propagation steps of an $S_{RN}1$ mechanism are presented in Scheme 1.

The wide variety of nucleophiles that can be used, the great functional group tolerance, and the fact that many carbon−carbon and carbon−heteroatom bonds can be obtained make the $S_{RN}1$ reaction a powerful synthetic tool.

SCHEME 1

$$(ArX)^{\bullet -} \longrightarrow Ar^{\bullet} + X^- \quad (1)$$

$$Ar^{\bullet} + Nu^- \longrightarrow (ArNu)^{\bullet -} \quad (2)$$

$$(ArNu)^{\bullet -} + ArX \longrightarrow ArNu + (ArX)^{\bullet -} \quad (3)$$

The $S_{RN}1$ mechanism has proved to be an important route to ring closure reactions, mainly in aromatic systems. The reaction of ortho-substituted aryl halides with different nucleophiles affords indoles, isocarbostyrils, binaphthyls, etc., and an important number of natural products have been achieved by this process.[2]

Ring closure reactions taking place by intramolecular addition of an aromatic radical to a double bond were widely studied with regard to both their regio- and stereochemical aspects. Many kinetics parameters are also known.[3] Aryl halides and diazonium salts substituted at the ortho-position with an *O*-allyl or *N*-allyl chain were used for the preparation of substituted and unsubstituted 2,3-dihydrobenzofuranes and 2,3-dihydro-1*H*-indoles under different reaction conditions. The general reaction pattern involves the generation of an aryl radical **1**•, which reacts with the double bond in a 5-exo trig fashion to afford the exocyclic radical **2**•, which can undergo reduction by a hydrogen donor to obtain the reduced cyclized product **2**-H[4] or reaction with different reagents to yield substituted product **2**-S[5] (Scheme 2).

(1) For reviews, see: (a) Rossi, R. A.; de Rossi, R. H. In *Aromatic Substitution by the $S_{RN}1$ Mechanism*; American Chemical Society: Washington, DC, 1983. (b) Norris, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed., Pergamon Press: 1991; Vol. 4, pp 451−482. (c) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1995; Supplement D2, Chapter 24, pp 1395−1485. (d) Rossi, R. A.; Pierini, A. B.; Santiago, A. N. In *Organic Reactions*; Paquette, L. A., Bittman, R., Eds.; Wiley & Sons: 1999; pp 1−271.

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(3) (a) Beckwith, A. L. J.; Gerba, W. B. *J. Chem. Soc., Perkin. Trans 2* **1975**, 593−600. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073−3099. (c) Beckwith, A. L. J.; Gerba, S. *Aust. J. Chem.* **1992**, *45*, 289−308. (d) Annunziata, A.; Galli, C.; Marinelli, M.; Pau, T. *Eur. J. Org. Chem.* **2001**, 1323−1329.

10.1021/jo026404m CCC: $22.00
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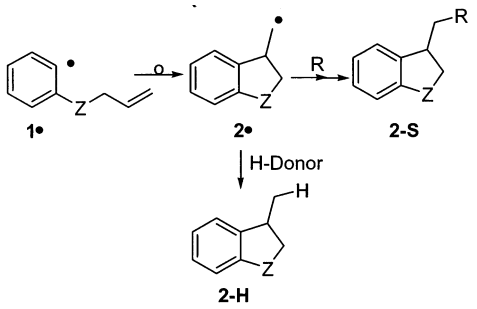
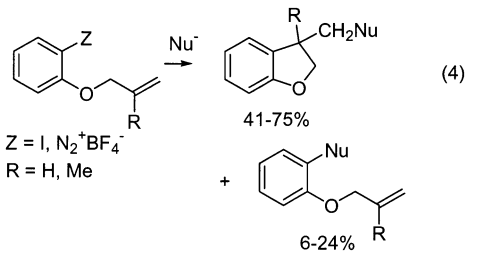
SCHEME 2



2-Allyloxy-1-bromo-naphthalene and 1-bromo-2-but-3-enyl-naphthalene afford products arising from both 5-exo and 6-endo cyclization (ratio 10:1) reactions, when refluxed with tributylstannane in benzene and in the presence of AIBN as an initiator (Scheme 3).[6] A neophyl rearrangement of the intermediate radical was demonstrated to be the process through which the 6-endo product is furnished. The fact that the uncyclized product is not formed indicates that the rate of H abstraction from tributylstannane is slower than the rate of cyclization.

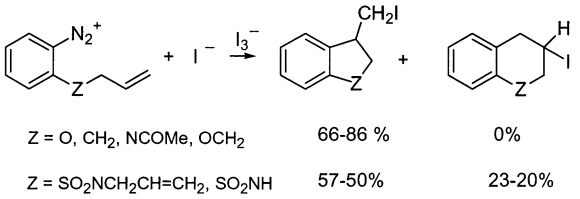
Although this general scheme was intensively employed for preparing heterocyclic compounds, there are only a few examples where the ring closure takes place in the propagation step of a $S_{RN}1$ reaction, and in most cases, the studies have been geared toward gathering kinetic information.[3d,7]

ArX and ArN_2^+ salts ortho-substituted with a radical probe offer the possibility of obtaining cyclic compounds by ET reaction with a nucleophile. In these systems, compounds arising from straightforward substitution may also be formed. Some examples of this approach are the reactions of 1-allyloxy-2-substituted benzene probes with PhS^-, Ph_2P^-,[7] PhS^-, *n*-BuS^-, $(EtO)_2CP^-$,[5b,g] and $MeCOS^-$ ions (eq 4).[5e]



(4)

Lower yields have been reported from reaction of the iodide-derived probe with *n*-$BuTe^-$ ions.[8] Good yields of cyclization are obtained by reaction of the *o*-(2-allyloxy)- and *o*-(2-but-3-enyloxy)benzene diazonium salts with ferrocene (65 and 49% yields, respectively) or mixtures of ferrocene and ferrocenium ions.[5f] On the other hand, the iododediazoniation is proposed to occur by the $S_{RN}1$ process (eq 5).[5c] Direct iodination or cyclization of the aromatic radical can result depending on the Z moiety. For example the latter reaction prevails when Z = $O(CH_2)_2$ or CO_2. When Z = $SO_2NCH_2CH{=}CH_2$ or SO_2NH, five- and six-membered fused ring products are formed (eq 5).[5c]



(5)

When the dediazoniation reaction of *o*-(3-but-3-enyloxy)benzene diazonium salts is performed in the presence of *n*-BuS^- or PhS^- ions in DMSO, 3-*n*-butyl (63%) and 3-phenyl (60%) sulfanylmethyl-2,3-dihydrobenzofuranes are obtained, respectively.[9]

Galli et al. used the radical clock approach in order to obtain kinetic data on the addition of pinacolone enolate anion to aromatic radicals.[3d] In this work, the reaction of 1-allyloxy-2-iodobenzene with pinacolone enolate anion in DMSO under irradiation is reported. One product obtained derives from direct coupling of the nucleophile with the aromatic ring; another aromatic substitution product arises from isomerization of the allylic moiety to the 1,2-position. These results were interpreted as a base-promoted isomerization of the double bond previous to the light-induced electron transfer, preventing in this way the ring closure in a 5-exo mode. Direct competition of an intramolecular process with the direct coupling of the nucleophile on the aromatic ring is not operative, since 4-exo and 5-endo cyclizations are highly disfavored.

The tandem cyclization−$S_{RN}1$ process competes with the attack of the nucleophile to the aryl radical before the ring closure reaction takes place. Absolute values of rate constants for the reactions of aryl radicals with nucleophiles have been determined electrochemically for a large number of cases. Most of these values are close to the diffusion limit. For instance, the rate constants for the coupling of 2-, 3-, or 4-cyanophenyl; 1-naphthyl; 3-pyridyl; and 3- and 4-quinolyl radicals with PhS^-, $(EtO)_2PO^-$, and $^-CH_2COMe$ ions range in the order of 10^9-10^{10} M^{-1} s^{-1} in liquid ammonia.[10]

Phenyl radicals appear to be less reactive than other aryl radicals, with rate constants for nucleophilic attack lower than the diffusion limit. The rate constants for the reactions of phenyl radicals with the previously men-

(4) Some representative examples can be found in ref 3c and in: (a) Beckwith, A. L. J.; Abeywikrema, A. N. *Tetrahedron Lett.* **1986**, *27*, 109−112. (b) Dittami, J. P.; Ramanathan, H. *Tetrahedron Lett.* **1988**, *29*, 45−48. (c) Boisvert, G.; Giasson, R. *Tetrahedron Lett.* **1992**, *33*, 6587−6590.

(5) Some representative examples can be found in: (a) Patel, V. F.; Pattenden, G.; Russel, J. J. *Tetrahedron Lett.* **1986**, *27*, 2303−2306. (b) Meijs, G. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5890−5893. (c) Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.* **1987**, *52*, 1922−1930. (d) Togo, H.; Kikuchi, O. *Tetrahedron Lett.* **1988**, *29*, 4133−4134. (e) Petrillo, G.; Novi, M.; Garbarino, G.; Filiberti, M. *Tetrahedron Lett.* **1988**, *29*, 4185−4188. (f) Beckwith, A. L. J.; Jackson, R. A.; Longmore, R. W. *Aust. J. Chem.* **1992**, *45*, 857−863. (g) Amatore, C.; Gareil, M.; Oturan, M. A.; Pinson, J.; Savéant, J.-M.; Thiébault, A. *J. Org. Chem.* **1986**, *51*, 3757−3761.

(6) Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 4072−4078.

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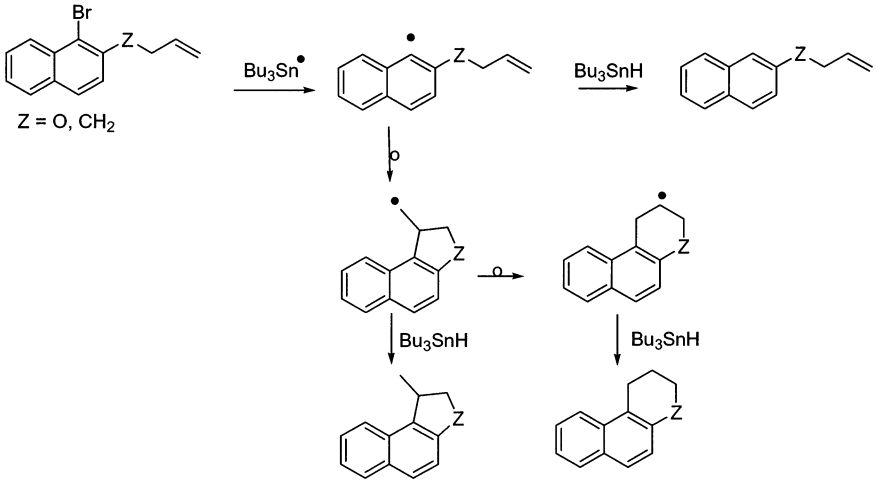
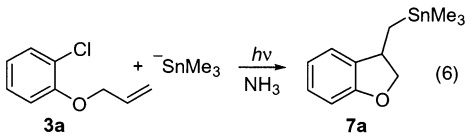
SCHEME 3



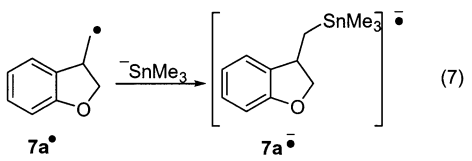
tioned nucleophiles are in the range 10^7-10^8 M^{-1} s^{-1}.[11] The rate constant for the ring closure reaction of *o*-allyloxy phenyl radical is 4.9×10^8 s^{-1} (in benzene, at 50 °C).[12] The fact that ring closure is a unimolecular process and, therefore, does not depend on nucleophile concentration as opposed to the bimolecular coupling reaction led us to the reasonable belief that, under controlled experimental conditions, the title compounds would be obtained in one-pot reactions by a tandem cyclization−$S_{RN}1$ sequence.

Results and Discussion

1-Allyloxy-2-chlorobenzene (**3a**) reacts with Me_3Sn^- ions in liquid ammonia under photostimulation to furnish cyclized-substituted compound **7a** in 87% yield (eq 6). The dark reaction under the same experimental conditions affords 2% yield of **7a**.



The results obtained indicate that an aryl free radical is an intermediate and that an $S_{RN}1$-type reaction is operating due to the nature of the product obtained and the lack of reaction under dark conditions (Table 1, entries 1 and 2). Upon irradiation, radical anion **3a**$^{-\bullet}$ is formed by ET from the nucleophile to **3a**. Fragmentation and rearrangement ensues to afford radical **7a**$^\bullet$, which ultimately furnishes product **7a** (eq 7).



(11) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846−4853.

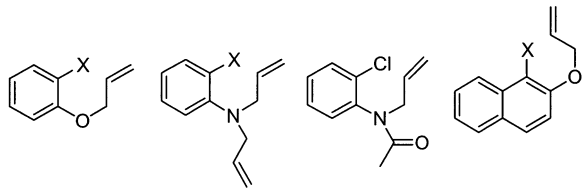
(12) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464−465.

TABLE 1. Photostimulated Reactions of 3−6 with Different Nucleophiles in Liquid Ammonia[a]

entry	substrate	nucleophile	product (yield, %)
1	**3a**	$^-SnMe_3$	**7a** (87)[b]
2[c]	**3a**	$^-SnMe_3$	**7a** (2)
3	**3a**	$^-PPh_2$	**7b** (73)
4[d]	**3a**	$^-PPh_2$	**7b** (75)
5	**3b**	$^-CH_2NO_2$[e]	**7c** (88)[f]
6	**4a**	$^-SnMe_3$	**8a** (97)[b]
7	**4a**	$^-PPh_2$	**8b** (80)
8	**4b**	$^-CH_2NO_2$[e]	**8c** (60)[f]
9	**5a**	$^-SnMe_3$	**9a** (97)[b]
10	**5a**	$^-PPh_2$	**9b** (76)
11	**6a**	$^-SnMe_3$	**10a** (84)
12	**6a**	$^-PPh_2$	**10b** (98)[b]
13	**6b**	$^-CH_2NO_2$[e]	**10c** (85)[f]

[a] Photostimulated reactions (2 h) were performed with 3.33×10^{-3} M substrate and 3.64×10^{-3} M nucleophile. Yields were determined by GC unless otherwise indicated. [b] Isolated product yield. [c] Dark conditions. [d] Concentration of the nucleophile was 16.7×10^{-3} M. [e] Nitromethane anion was 20.0×10^{-3} M together with 3.33×10^{-3} M acetone enolate anion as the entrainment reagent. Irradiation time was 3 h. [f] A small quantity of reduced product was also detected by CG-MS, but was not isolated or quantified.

CHART 1

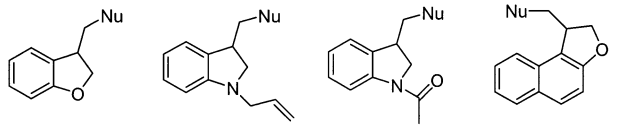


3a, X=Cl **3b**, X=Br | **4a**, X=Cl **4b**, X=Br | **5a** | **6a**, X=Cl **6b**, X=Br

Under our reaction conditions, products arising via direct coupling of the nucleophile with the aryl radical **3a**$^\bullet$ were not detected, probably due to the low concentration of reactants employed.

To extend this study to the synthesis of other heterocyclic compounds, *N*-allyl-(2-chloro-phenyl)-amine, *N*,*N*-diallyl-(2-chlorophenyl)-amine (**4a**), *N*-allyl-*N*-(2-chlorophenyl)-acetamide (**5a**), and 2-allyloxy-1-chloronaphthalene (**6a**) (Chart 1) were prepared and tested under similar reaction conditions with Me_3Sn^- ions.

CHART 2



7a, Nu=$SnMe_3$ **8a**, Nu=$SnMe_3$ **9a**, Nu=$SnMe_3$ **10a**, Nu=$SnMe_3$
7b, Nu =$P(O)Ph_2$ **8b**, Nu=$P(O)Ph_2$ **9b**, Nu=$P(O)Ph_2$ **10b**, Nu=$P(O)Ph_2$
7c, Nu=CH_2NO_2 **8c**, Nu=CH_2NO_2 **10c**, Nu=CH_2NO_2

There are only a few examples of radical ring closure reactions using *N*-allylaniline derivatives,[5d,4b,8] and rate constants for this 5-exo trig process are not known.

When *N*-allyl-(2-chloro-phenyl)-amine is allowed to react with Me_3Sn^- ions in liquid ammonia, a low yield of 3-trimethylstannanylmethyl-2,3-dihydro-1*H*-indole is obtained (ca. 30% yield, see Experimental Section, compound **8d**). This low yield can be attributed to the acidity of the starting substrate, which is likely to undergo deprotonation in the highly basic reaction medium. We therefore decided to protect the amine group, as depicted in compounds **4a**,**b** and **5a** in Chart 1.

Compounds **8a**, **9a**, and **10a** (Chart 2) were obtained from the photostimulated reactions with Me_3Sn^- ions in high yields (Table 1, entries 6, 9, and 11), uncontaminated with products arising from direct coupling of the nucleophile with the aromatic radical. Neither products of reduction nor products of 6-endo cyclization were observed.

The aromatic radical **4a•**, formed as an intermediate, reacts with one of the tethered double bonds in a 5-exo process to form radical **8a•** (N-analogue of **7a•** in eq 7); this resulting radical could either react with the nucleophile to produce the observed substitution product **8a** or ring-close further in a 6-exo or 7-endo trig fashion with the remaining allyl moiety as a competitive pathway. However, no products from 6-exo or 7-endo cyclizations were observed. The high reactivity of Me_3Sn^- ions and the fact that both exo and endo ring closure are very disfavored account for the results obtained.

When substrate **5a** is brought into reaction with Me_3Sn^- ions, almost a quantitative yield of product **9a** is obtained. Despite the strong basicity observed for Me_3Sn^- ions,[13] the acetyl moiety probably does not undergo an acid−base process. Instead, tandem cyclization and $S_{RN}1$ nucleophilic substitution occurs.

In the photostimulated reaction of **6a** with Me_3Sn^- ions, no product derived from 6-endo cyclization was detected. Probably the nucleophile reacts faster with the intermediate radical **10a•** to afford the radical anion of the observed substituted product **10a**, in which case the neophyl rearrangement cannot effectively compete, as has been previously reported.[6]

Encouraged by the results obtained with the tin nucleophile, we undertook the study employing Ph_2P^- ions, as these anions have been extensively investigated in aromatic $S_{RN}1$ substitutions.[1] Previous to analyses, all reaction mixtures were first treated with 10% H_2O_2 solution to convert the relatively unstable phosphines that could have been formed into their more stable phosphine oxides. After 120 min of irradiation of liquid ammonia solutions of Ph_2P^- ions with substrates **3a**−**6a** and subsequent treatment with the peroxide solution, the corresponding phosphine oxides were obtained in very good yields (Table 1, entries 3, 7, 10, and 12).

The fact that we did not detect uncyclized products and that all the products arise from 5-exo cyclization clearly show the difference in rate constants between the 5-exo cyclization compared with the 6-exo cyclization process and the attack of the nucleophile to the aromatic radical.[7]

To appraise whether the aromatic-centered radical could be trapped by Ph_2P^- ions, we carried out the reaction with a 5-fold increase in nucleophile concentration (Table 1, entry 4); however, no *ipso* substitution product was observed.

Given the discouraging results obtained from the reaction of the enolate ion of pinacolone (a standard $S_{RN}1$ carbanion) and 1-allyloxy-2-iodobenzene in DMSO,[3d] we undertook the study of the reactions of nitromethane anion. It is known that acetone enolate anion does not react with primary alkyl radicals and that nitromethane anion is not capable of initiating the $S_{RN}1$ reactions even under irradiation.[14] Leaving group chlorine (in substrates **3a**, **4a**, and **6a)** was replaced with the more reactive bromine (substrates **3b**, **4b**, and **6b**) and tested in irradiated liquid ammonia solutions using nitromethane anion as a nucleophile and acetone enolate anion as an entrainment reagent (which enables $S_{RN}1$ initiation but cannot compete with the coupling of the methylene radical with nitromethane anion after cyclization).

The results obtained are summarized in Table 1 (entries **5**, **8**, and **13**). Yields can be regarded as good to satisfactory. These reactions result in two C−C bonds being formed. The nitro groups in the tethered chains render the products obtained interesting for further synthetic transformations (a nitro group can be readily transformed into a number of other useful functional groups,[15] which extends the synthetic scope of these reactions).

It is likely that the low temperature in the liquid ammonia solutions is a decisive factor, playing a role in governing the lack of isomerization of the double bond on the allylic chain, as was indeed observed in DMSO solution. In our reactions, unreacted substrates together with reduced products were also detected, albeit in small amounts.

Conclusions

Dihydrobenzofuranes and dihydroindoles substituted with different groups at the 3-position were prepared from ortho-functionalized haloaromatic compounds by the $S_{RN}1$ mechanism using Ph_2P^-, Me_3Sn^-, and nitromethane ions as nucleophiles.

The products were obtained in high yields, and the reactions are clean, since only products from ring closure and substitution were formed. The operating mechanism is the $S_{RN}1$ in which, during the propagation cycle, a fast

(13) A pK_a value of 23.5 for trimethylstannane was reported: Petrov, E. S.; Terekhova, M. I.; Mirskov, R. G.; Voronkov, M. G.; Shatenstein, A. I. *Dokl. Akad. Nauk. SSSR* **1975**, *221*, 111; *Chem. Abstr.* **1975**, *8*, 155040.

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regioselective 5-exo ring closure takes place giving an alkyl radical that finally reacts with the nucleophiles. The chosen solvent and the dilute reaction conditions make competitive side reactions unimportant. The high reactivity of the employed nucleophiles and the high rate constant for the 5-exo cyclization satisfactorily explain the observed product distributions.

In all reactions studied, at least one carbon−carbon bond was formed and the products obtained are interesting because they are plausible for further synthetic transformation.

Experimental Section

General Methods. The internal standard method was used for quantitative GC analysis using authentic samples, and one of the following columns was employed: HP-1 (5 m × 0.53 mm ID) or HP-1 (30 m × 0.32 mm ID column). ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.32 MHz) were conducted in deuteriochloroform as a solvent unless otherwise indicated. Coupling constants (*J*) are given in hertz. High-resolution mass spectrometric measurements were conducted at Universidade de Santiago de Compostela, Unidade de Espectrometría de Masas. GC/MS analyses were carried out on a Shimadzu QP-5050 apparatus coupled with a mass selective detector and a DB-5 (30 m × 0.25 mm ID) capillary column.

Materials. Trimethyl tin chloride, triphenylphosphine, nitromethane, and potassium *t*-butoxide were obtained from commercial sources. Acetone and nitromethane were double distilled and stored under nitrogen over molecular sieves (4 Å). 2-Chlorophenol, 2-bromophenol, 2-chloroaniline, 2-bromoaniline, 1-chloro-2-naphthol, 1-bromo-2-naphthol, and allyl bromide used to prepare substrates were commercially available. Silica gel (0.063−0.200 mm) was used in column chromatography and 2 mm plates (silica gel 60 PF_{254}) in radial thin-layer chromatography purification. All solvents were analytical grade and used as received from the supplier. 1-Allyloxy-2-chlorobenzene[4c] (**3a**), 1-allyloxy-2-bromo-benzene[4c] (**3b**), *N*,*N*-diallyl-(2-bromo-phenyl)-amine[16] (**4b**), and 2-allyloxy-1-bromo-naphthalene[6] (**6b**) were prepared as previously reported.

***N*-Allyl-(2-chloro-phenyl)-amine, *N*,*N*-Diallyl-(2-chloro-phenyl)-amine (4a), and *N*-Allyl-*N*-(2-chloro-phenyl)-acetamide (5a).** To a round-bottomed flask equipped with a reflux condenser and magnetic stirring were added *o*-chloroaniline (20 mmol) and allyl bromide (50 mmol). The mixture was heated at 80 °C overnight and cooled to ambient temperature. Sodium hydroxide solution was added until the medium was basic, and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The organic phase was dried over magnesium sulfate and evaporated in a vacuum. The crude was poured into a two-necked round-bottomed flask equipped with magnetic stirring and a reflux condenser, and acetic anhydride was then added in excess. The mixture was boiled for 2 h before water was added in excess, and the new mixture was boiled for an additional 2 h. The aqueous phase was extracted with dichloromethane (3 × 50 mL). The organic layers were dried (magnesium sulfate) and evaporated. Compounds **4a** (40% yield) and **5a** (55% yield) were separated by silica gel column chromatography using hexane and acetone. For the isolation of *N*-allyl-(2-chloro-phenyl)-amine, the crude mixture of amines (*N*-allyl-(2-chloro-phenyl)-amine and **4a**) was not acetylated but carefully chromatographed on silica gel with hexane to yield, after evaporation, **4a** and *N*-allyl-(2-chloro-phenyl)-amine as pure colorless liquids (40 and 50% yields, respectively). Spectral data for *N*-allyl-(2-chloro-phenyl)-amine[17a] and **5a**[17b] match well with those previously reported. Product **4a** was characterized by standard spectroscopic techniques as follows. ^{1}H NMR ($CDCl_3$) δ_H: 4.37 (br d, 4 H); 5.80 (cplx. m, 4 H); 6.46 (12 lines, 2 H); 7.68 (cplx. m, 3 H); 7.99 (dd, 1 H, J = 7.9, 3). ^{13}C NMR ($CDCl_3$) δ_c: 54.75; 117.39; 123.31; 123.42; 126.70; 129.61; 130.53; 134.70; 147.65. GC/MS EI, *m*/*z* (%): 41 (100), 51 (19), 75 (35), 77 (33), 111 (59), 130 (87), 137 (75), 140 (31), 164 (16), 172 (92), 180 (75), 182 (23), 207 (44), 209 (16). DEI-HRMS calcd for $C_{12}H_{14}ClN$, 207.0815; found, 207.0812.

2-Allyloxy-1-chloro-naphthalene (6a). Into a round-bottomed flask equipped with a reflux condenser and under magnetic stirring were added DMF (15 mL), 1-chloro-2-naphthol (13 mmol), allyl bromide (19 mmol), and sodium carbonate (19 mmol). The reaction mixture was heated at 80 °C overnight; after cooling, water was added (50 mL), and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The organic layer was dried (magnesium sulfate) and the solvent evaporated, and the crude was purified by silica gel column chromatography using hexane/ethyl ether to yield 90% of pure **6a** as a yellow solid (mp 42−44 °C), which was characterized by standard spectroscopic techniques as follow. ^{1}H NMR ($CDCl_3$) δ_H: 4.75 (dt, 2 H, J = 1.6, 5.2); 5.36 (d q, 1 H, J = 3, 5.8, 10.5); 5.54 (dq, 1 H, J = 3.3, 6.5, 17.2); 6.15 (10 lines, 1 H, J = 5.2, 10.2); 7.25 (d, 1 H, 17.8); 7.44 (cpx. m, 1 H); 7.61 (cplx. m, 1 H); 7.77 (br m, 1 H); 8.31 (br d, 1 H). ^{13}C NMR ($CDCl_3$) δ_c: 70.49; 115.38; 117.72; 123.43; 124.32; 127.26; 127.67; 127.88; 129.59; 131.82; 132.86; 151.62. GC/MS EI, *m*/*z* (%): 41 (19), 63 (12), 114 (28), 149 (100), 151 (33), 177 (45), 218 (34). DEI−HRMS calcd for $C_{13}H_{11}ClO$, 218.0498; found, 218.0478.

Reactions of 3a, 4a, 5a, and 6a with Me_3Sn^- Ions in Liquid Ammonia. Into a three-necked, 500 mL round-bottomed flask equipped with a coldfinger condenser charged with ethanol, a nitrogen inlet, and a magnetic stirrer were condensed 300 mL of ammonia, previously dried with Na metal, under nitrogen. Me_3SnCl (1.10 mmol) was then added, and Na metal (2.65 mmol) in small pieces was introduced, waiting for total decoloration between each addition. A lemon yellow solution of Me_3Sn^- ions is obtained. The substrates were dissolved in 1 mL of dried ethyl ether and added to the solution. The reaction mixture was irradiated for 120 min using two medium-pressure mercury lamps emitting maximally at 366 nm. The reaction was quenched by adding ammonium nitrate in excess. The ammonia was allowed to evaporate, and water (50 mL) was added. The aqueous phase was extracted with dichloromethane (3 × 50 mL), and the organic phase was dried (magnesium sulfate) and the solvent evaporated in vacuo. The products were purified as indicated.

Reactions of 3b, 4b, and 6b with Ph_2P^- Ions in Liquid Ammonia. These reactions were performed in a fashion similar to those with Me_3Sn^- ions, but 1.10 mmol of Ph_3P was added instead and then Na metal (2.65 mmol) in small pieces. The addition of Na metal continued until the blue solution from solvated electrons in excess remained colored for an additional 20 min before it became orange-brown and no more solid was present. To this solution was added *t*-BuOH (1.10 mmol) to neutralize the amide ion formed. Previous to drying, the dichloromethane phase was treated with 10% H_2O_2 (50 mL) and then water (50 mL). Products were purified as indicated.

Reactions of 3b, 4b, and 6b with Nitromethane Anion in Liquid Ammonia. These reactions were performed by a procedure similar to that described for the other two nucleophiles, but 6 mmol of nitromethane, 1 mmol of acetone, and 7.7 mmol of *t*-BuOK were added, waiting 15 min for the formation of the nucleophile and the entrainment reagent. A slightly colored solution was obtained. The reactions were irradiated for 180 min.

(2,3-Dihydro-benzofuran-3-ylmethyl)-trimethyl-stannane (7a). Spectral data for this compound have previously been reported.[18]

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3-(Diphenyl-phosphinoylmethyl)-2,3-dihydro-benzofuran (7b): white solid, mp 123−124 °C, purified by column chromatography with a 50/50 hexane/ethyl acetate mixture as the solvent. ^{1}H NMR ($CDCl_3$) δ_H: 2.56 (d t, 1 H, J = 10.6, 15); 2.77 (q d, 1H, J = 3.3, J = 9.5, 10.2); 3.83 (br m, 1 H); 4.27 (dd, 1 H, J = 9.1, 9.5); 4.56 (t, 1 H, J = 8.8, 9.5); 6.80 (octet, 2 H); 7.11 (cplx. t, 2 H); 7.52 (br cplx. m, 6 H); 7.78 (br cplx. m, 4 H). ^{13}C NMR ($CDCl_3$) δ_C: 35.40 (d, ^{P-C}J = 69); 36.28 (d, J = 4); 109,77; 120.61; 123.92; 128.67; 128.73; 128.77; 128.94; 130.58; 130.71; 130.90; 132.01; 132.06; 159.55. GC/MS EI, *m*/*z* (%): 47 (21), 65 (9), 77 (38), 91 (19), 125 (19), 131 (19), 155 (28), 183 (9), 202 (88), 215 (100), 216 (60), 317 (0.5), 334 (12). DEI-HRMS calcd for $C_{21}H_{19}O_2P$, 334.1123; found, 334.1119.

3-(2-Nitro-ethyl)-2,3-dihydrobenzofuran (7c): obtained as a colorless liquid, purified by radial thin-layer chromatography with hexane. ^{1}H NMR ($CDCl_3$) δ_H: 2.44 (cplx. m, 2 H); 3.60 (br quintet, 1 H); 4.23 (q, 1 H, J = 4.8, 9); 4.42 (t, 2 H, J = 7.3); 4.60 (d t, 1 H); 6.91 (d, 1 H, J = 8.1); 6.99 (d t, 1 H, J = 7.7, 7.3); 7.27 (cplx. m, 2 H). ^{13}C NMR ($CDCl_3$) δ_C: 32.13; 38.94; 72.98; 75.84; 109.99; 120.80; 121.96; 128.29; 129.02; 159.69. GC/MS EI, *m*/*z* (%): 65 (27), 77 (9), 91 (100), 119 (35), 145 (16), 193 (12). DEI-HRMS calcd for $C_{10}H_{11}NO_3$, 193.0739; found, 193.0734.

1-Allyl-3-trimethylstannanylmethyl-2,3-dihydro-1*H*-indole (8a): colorless liquid obtained in 97% yield by column chromatography with hexane. ^{1}H NMR (CD_3COCD_3) δ_H: 0.067 (s s, 9H, $^{CH_3-Sn}J$ = 13); 1.02−0.89 (cplx. m, 1 H); 1.20 (cplx. m, 1 H, J = 1.1, 7); 1.33 (br s, 1 H); 1.46 (t d, 1 H, J = 2.6, 4.4,); 2.95−2.78 (cplx. m, 1 H); 3.56 (cplx. m, 2 H); 3.74 (q t, 2 H, J = 1.46, 6.2); 3.75 (q t, 1 H, J = 1.1, 6.2, 13.9); 5.21 (cplx. d quintet, 1 H, J = 1.46, 3.6,10.2); 5.32 (d q, 1 H, J = 1.46, 3.3, 17.1); 5.96 (q t, 1 H, J = 5.8, 6.2, 10.2, 17.1), 6.54 (d, 1 H, J = 7.7); 6.65 (d t, J = 1.1, 7.7); 7.03 (br t, 2 H). ^{13}C NMR (CD_3COCD_3) δ_C: −9.23 (t, J = 161); 17.29; 39.57; 52.41; 62.61; 108.20; 117.49; 118.49; 123.97; 128.05; 135.33; 137.21; 152.51. GC/MS EI, *m*/*z* (%): 77 (15), 91 (88), 103 (9), 117 (9), 130 (81), 131 (11), 170 (100), 172 (38), 320 (isotopic cluster, 21), 337 (isotopic cluster, 3). DEI-HRMS calcd for $C_{14}H_{20}N^{120}Sn$ (M^+ − 15), 322.0618; found, 322.0624.

1-Allyl-3-(diphenyl-phosphinoylmethyl)-2,3-dihydro-1*H*-indole (8b): obtained as an off-white oil, purified by column chromatography with a 50/50 hexane/ethyl acetate mixture. ^{1}H NMR ($CDCl_3$) δ_H: 2.70 (cplx. m, 2 H); 3.13 (cplx. m, 1 H); 3.43−3.82 (cplx. m, 3 H); 5.12 (cplx. d, 1 H, J = 1.1, 9.8); 5.23 (cplx. t, 1 H, J = 1.4, 3); 6.1−5.71 (cplx. m, 2 H); 6.48 (d, 1 H, J = 7.7); 6.64 (t, 1 H, J = 7.3); 7.05 (cplx. m, 2 H); 7.50 (br cplx. m, 6 H); 7.78 (br cplx. m, 4 H). ^{13}C NMR ($CDCl_3$) δ_C: 34.86 (d, J = 70); 51.56; 59.50 (d, J = 3); 64.2; 107.56; 113.57; 117.51; 117.55; 123.22; 127.99; 128.56; 128.64; 128.78; 128.88; 130.53; 130.72; 130.90; 131.79; 133.60; 151.50. GC/MS EI, *m*/*z* (%): 65 (3), 77 (21), 91 (10), 130 (27), 170 (55), 171 (62), 183 (6), 201 (7), 215 (100), 216 (39), 277 (9), 373 (7). DEI-HRMS calcd for $C_{24}H_{24}NOP$, 373.1596; found, 373.1599.

1-Allyl-3-(2-nitro-ethyl)-2,3-dihydro-1-*H*-indole (8c): slightly yellow oil, purified by radial thin-layer chromatography with hexane. ^{1}H NMR ($CDCl_3$) δ_H: 2.37 (d sextet, 2 H, J = 6.9, 7.3, 14, 23), 3.11 (q, 1 H, J = 4.7, 8.7); 3.31 (br q, 1 H); 3.50 (s t, 1 H, J = 8.4), 3.72 (cplx. m, 2 H); 4.46 (d t, 2 H, J = 7.3, 9.1); 5.27 (d q, 1 H, J = 1.4, 3.3), 5.26 (cplx. m, 1 H); 5.90 (quadrup. t, 1 H, J = J = 5.8, 10.2, 23); 6.55 (d, 1 H, J = 8); 6.72 (d t, 1 H, J = 0.7, 7); 7.13 (cplx. m, 2 H). ^{13}C NMR ($CDCl_3$) δ_C: 31.67; 37.49; 51.61; 58.40; 73.36; 107.75; 117.56; 117.94; 123.92; 128.32; 131.04; 133.62; 151.60. GC/MS EI, *m*/*z* (%): 63 (2), 77 (1); 89 (4), 117 (63), 130 (53), 158 (100), 170 (2), 232 (40). DEI-HRMS calcd for $C_{13}H_{16}N_2O_2$, 232.1212; found, 232.1205.

3-Trimethylstannanylmethyl-2,3-dihydro-1*H*-indole (8d): slightly yellow oil, purified by radial thin-layer chromatography with hexane and obtained in 30% yield. ^{1}H NMR (CD_3COCD_3) δ_H: 0.072 (ss, 9 H, ^{Sn-H}J = 1.46, 27); 150−1.43 (cplx. m, 2 H); 3.08 (br t, 1 H, J = 6.9); 3.73−3.52 (cplx. m, 2 H); 4.74 (br s, 1 NH); 6.63 (cplx. q; 2 H); 6.95 (t t, 1H, J = 0.74, 6.9); 7.06 (1 H, br d, J = 7.3). ^{13}C NMR (CD_3COCD_3) δ_C: −9.61; 17.16; 40.76; 56.53; 109.42; 118.08; 123.71; 127.58; 135.69; 152.51. δ_C DEPT 135: (CH_2) 17.16; 56.58. CH: 40.76; 109.41; 118.09; 123.75; 127.58. GC/MS EI, *m*/*z* (%): 41 (6), 77 (17), 91 (9), 106 (15), 117 (isotopic cluster, 15), 130 (100), 132 (98), 208 (isotopic cluster, 6), 224 (isotopic cluster, 12), 250 (isotopic cluster, 25), 280 (isotopic cluster, 42), 297 (M^+, isotopic cluster, 5). DEI-HRMS calcd for $C_{12}H_{19}N^{120}Sn$, 297.0539; found 297.0537.

1-(3-Trimethylstannanylmethyl-2,3-dihydro-indol-1-yl)-ethanone (9a): white solid, mp 73−74 °C, obtained in 97% yield by column chromatography with a 75/25 hexane/dichloromethane mixture. ^{1}H NMR ($CDCl_3$) δ_H: 0.04 (ss, 9 H, $^{CH_3-Sn}J$ = 26.4, 1.1); 1.28 (cplx. m, 2 H, J = 8.4, 4.4); 2.20 (s s, 3 H); 3.49 (cplx. m, 1 H); 3.71 (br cplx. m, 1 H); 4.18 (br t, 1 H, J = 9.5); 7.02 (d t, 2 H, J = 1.1, 7.7); 7.15 (d q, 2 H, J = 1.1, 8.4); 8.18 (b d, 2 H, J = 8). ^{13}C NMR ($CDCl_3$) δ_C: −9.49 ($^{H_3C-Sn}J$ = 163, 6.7); 18.35; 24.15; 38.38; 57.81; 116.97, 123.44; 123.74; 127.68; 137.40; 142.12; 168.43. GC/MS EI, *m*/*z* (%): 43 (91), 77 (24), 91 (13), 103 (16), 117 (39), 130 (89), 132 (79), 165 (25), 174 (100), 324 (isotopic cluster, 37), 339 (2). DEI-HRMS: calcd for $C_{13}H_{18}NO^{120}Sn$ (M^+ −15), 324.0410; found, 324.0416.

1-[3-(Diphenyl-phosphinoylmethyl)-2,3-dihydro-indol-1-yl]-ethanone (9b): white solid, mp 102−104 °C, purified by recrystallization in a ca. 80/20 hexane/acetone mixture. ^{1}H NMR ($CDCl_3$) δ_H: 2.11 (ss, 3 H); 2.55 (sextet, 1 H); 2.77 (dq, 1 H, J = 3, J = 9, J = 12); 3.74 (br cplx. m, 1 H); 3.95 (dd, 1 H, J = 5.5); 4.15 (cplx. t, 1 H); 7.10 (cplx. m, 3 H), 7.52 (br cplx. m, 7 H); 7.78 (cplx. m, 3 H), 8.16 (b d, 1 H, J = 8). ^{13}C NMR ($CDCl_3$) δ_C: 24.09; 34.82; 35.67 (d, J = 70); 54.95; 117.16; 123.28; 123.74; 128.45; 128.80; 128.91; 129.04; 129.15; 130.47; 130.72; 130.90; 132.20; 142.33; 168.96. GC/MS EI, *m*/*z* (%): 47 (12), 77 (14), 91 (7), 130 (33), 174 (6), 202 (10), 215 (100), 216 (61), 375 (3). DEI-HRMS calcd for $C_{23}H_{22}NO_2P$, 375.1388, found, 375.1385.

(1,2-Dihydro-naphtho[2,1-*b*]furan-1-ylmethyl)-trimethyl-stannane (10a): colorless oil purified by radial thin-layer chromatography with hexane. ^{1}H NMR ($CDCl_3$) δ_H: −0.09 (s s, 9 H, ^{H-Sn}J = 26); 1.28−1.6 (cplx. m, 2 H); 4.21 (cplx. m, 2 H); 4.75 (b t, 1 H, J = 8.8): 7.08 (d, 1 H, J = 8.8); 7.29 (br d, 1 H); 7.44 (br t, 1 H, J = 6.9); 7.71 (sextet, 3H). ^{13}C NMR ($CDCl_3$) δ_C: −9.87; 18.19; 39.62; 79.53; 112.20; 122.23; 122.58; 124.60; 126.43; 128.91; 129.61; 130.34; 156.56. GC/MS EI, *m*/*z* (%): 51 (6), 63 (8), 77 (9), 115 (23), 135 (cluster, 14), 141 (cluster, 27), 152 (cluster, 42), 165 (60), 183 (cluster, 100), 333 (cluster, 38), 349 (cluster, 4). DEI-HRMS calcd for $C_{16}H_{20}O^{120}Sn$, 348.0536; found, 348.0534.

1-(Diphenyl-phosphinoylmethyl)-1,2-dihydro-naphtho-[2,1-*b*]furan (10b): white solid, mp 156−158 °C, obtained in 97% yield by recrystallization in a ca. 80/20 hexane/acetone mixture. ^{1}H NMR ($CDCl_3$) δ_H: 2.70 (13 lines, 2 H); 4.14 (br cplx. m, 1 H); 4.58 (t, 1 H, J = 8.4); 4.73 (dd, 1 H, J = 2.6, 9.5); 7.09 (d, 1 H, J = 8.8); 7.93−7.29 (cplx. m, 15 H). ^{13}C NMR ($CDCl_3$) δ_C: 35.10 (d, ^{C-P}J = 69); 36.26 (d, J = 4); 76.87 (d, J = 3); 109.75; 120.61; 123.90; 128.64; 128.68; 128.75; 128.93; 128.98; 130.54; 130.70; 130.73; 130.88; 132.01; 132.04; 159.55. GC/MS EI, *m*/*z* (%): 47 (14), 77 (12), 115 (15), 152 (19), 182 (100), 202 (28), 215 (47), 384 (14). DEI-HRMS calcd for $C_{25}H_{21}O_2P$, 384.1279; found 384.1276.

1-(2-Nitro-ethyl)-1,2-dihydro-naphtho[2,1-b]furan (10c): slightly yellow oil, purified by radial thin-layer chromatography with hexane. ^{1}H NMR ($CDCl_3$) δ_H: 2.39 (10 lines, 1 H, J = 6.2, 7.7); 2.61 (10 lines, 1 H, J = 4.0, 14.6, 18.3); 3.94 (br septet, 1 H); 4.41 (14 lines, 3 H); 4.71 (t, 1 H, J = 9); 7.12 (d, 1 H, J = 8.8); 7.34 (cplx. t, 1 H); 7.52 (cplx. t, 1 H); 7.75 (cplx. m, 3 H). ^{13}C NMR ($CDCl_3$) δ_C: 31.05; 38.59; 72.93; 76.22; 112.17; 119.61; 121.79; 123.22; 127.29; 129.13; 129.64; 130.20; 130.29; 157.40. GC/MS EI, *m*/*z* (%): 63 (5), 89 (4), 115 (31), 141 (77), 169 (100), 181 (14), 196 (16), 243 (28). DEI-HRMS calcd for $C_{14}H_{13}NO_3$, 243.0895; found, 243.0903.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **4a**, **6a**, **7a**−**c**, **8a**−**c**, **9a**,**b**, and **10a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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