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THE SYNTHESIS OF BIS(PHENYLSELENENYL), BIS(ALKYLSELENENYL)PYRIDINES AND OF PYRIDYLSELENOLATE ANIONS

Marcello Tiecco,* Lorenzo Testaferri,* Marco Tingoli, Donatella Chianelli, Donatella Bartoli, and Roberta Balducci

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, Italy.

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Abstract. The reactions of several dihalogenopyridines with PhSeNa or MeSeLi in DMF afforded the monosubstitution products in good yields. With excess PhSeNa the bis(phenylselenenyl)pyridines were easily obtained, whereas with excess MeSeLi the initially formed halogenopyridyl methyl selenides, rather than aromatic substitution, suffered dealkylation to give the halogenopyridyl selenolate anions, as a result of an S_N2 substitution process. Addition of i-propyl iodide afforded the halogenopyridyl i-propyl selenides. Treatment of these compounds with excess MeSeLi gave the (i-propylselenenyl)pyridylselenolate anions which were directly treated with an alkylating agent and good yields of bis(alkylselenenyl)pyridines were obtained. All these nucleophilic aromatic substitution reactions were completely regiospecific.

In previous papers we have shown that nucleophilic aromatic substitution reactions, which occur with the classical addition - elimination mechanism, can be easily effected even on unactivated aryl halides simply by working in dipolar aprotic solvents (HMPA, DMF, DMA). In the same solvents, selective dealkylations of the obtained products can be effected by substitution, elimination or electron transfer reactions.[1-11] Thus, using oxygen, sulphur or selenium nucleophiles and starting from aryl halides, very simple and efficient methods have become available for the synthesis of ethers,[2] thioethers,[1,3,6,8] selenoethers,[11,12] substituted phenols,[2,7,10] thiophenols,[1,4,7] selenophenols,[11] poly(mercapto)benzenes,[9] and poly(seleno)benzenes.[11] These synthetic methods have already found several applications.[13-17] Recently, the reactions with sulphur and oxygen nucleophiles have been successfully used in the pyridine series.[18]

We now report the results of a related investigation carried out on some halogenopyridines in order to find the experimental conditions to introduce one or two selenium containing groups into the pyridine nucleus:

$$C_5H_3NX_2 \xrightarrow[X = Cl,Br]{RSe^-} C_5H_3NX(SeR) \xrightarrow[R = Ph,Me]{RSe^-} C_5H_3N(SeR)_2$$

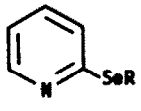
Because of the simple procedure employed and of the high yields obtained, the method now described compares favourable with the few other syntheses reported in the literature [19-24] and can give a contribution to the growing synthetic applications of organoselenium compounds.[25]

RESULTS AND DISCUSSION

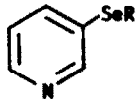
The substrates employed for the present investigation were the commercially available 2-bromo-, 1, 3-bromo-, 2, 4-chloro-, 3, 2,6-dibromo-, 4, 2,5-dibromo-, 5, 2,3-dichloro-, 6, and 3,5-dichloropyridine, 7. These compounds were allowed to react in DMF with PhSeNa and MeSeLi prepared from diphenyl diselenide and sodium hydride and from methyllithium and elemental selenium, respectively. The reactions with PhSeNa proceeded smoothly, whereas those with MeSeLi gave rise to some complications which will be discussed below and required controlled experimental conditions. Reaction yields of isolated products are reported in parentheses in Schemes 1-5.

The reactions of the monohalogenopyridines, 1-3, with PhSeNa (1,2 molar equivalents) were carried out at 80 °C and afforded the 2-, 3-, and 4-phenylselenenylpyridine, 8, 9, and 10 (Scheme 1). As expected, the substitution process required much longer reaction times in the case of 3-bromopyridine. Under the same conditions the dihalogenopyridines were converted into the phenylselenenyl halogenopyridines 14 - 17 (Scheme 1) slightly contaminated by the bissubstituted products; these, however, could be easily separated by column chromatography. As expected, the substitution reactions regioselectively occurred at the 2 position in the case of compounds 5 and 6. In order to minimize the formation of the bissubstituted product the reaction of 4 was carried out at lower temperature (50 °C). The bis(phenylselenenyl)pyridines 22 - 25 (Scheme 1) were easily obtained from 4 - 7 using an excess (4 mol) of PhSeNa at 120 °C. Thus all the possible substitution products of halogenopyridines with PhSe can be obtained in good yields using the extremely simple procedure here described.

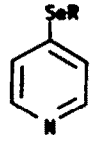
SCHEME 1



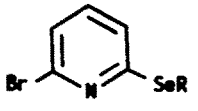
8 : R = Ph (67%)
11 : R = Me (72%)



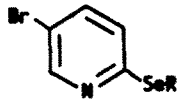
9 : R = Ph (62%)
12 : R = Me (66%)



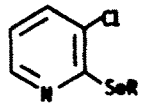
10 : R = Ph (62%)
13 : R = Me (58%)



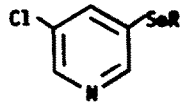
14 : R = Ph (83%)
18 : R = Me (92%)



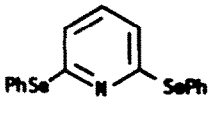
15 : R = Ph (87%)
19 : R = Me (72%)



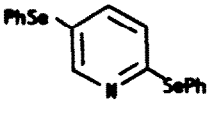
16 : R = Ph (76%)
20 : R = Me (90%)



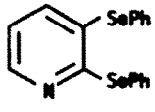
17 : R = Ph (54%)
21 : R = Me (87%)



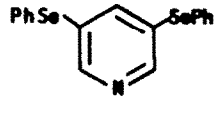
22 (70%)



23 (87%)



24 (95%)

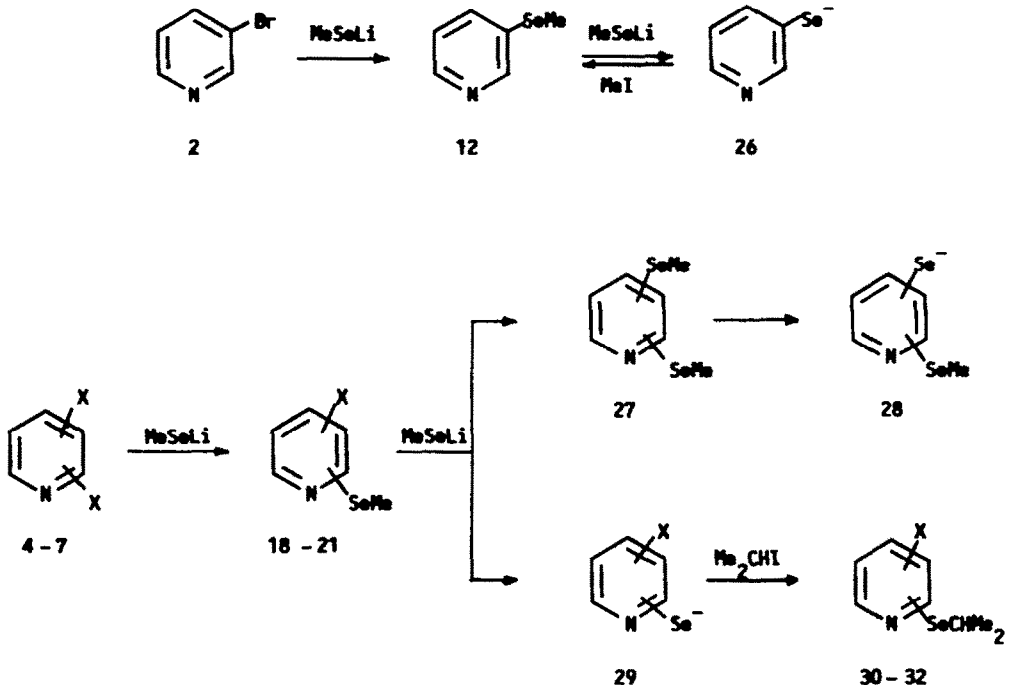


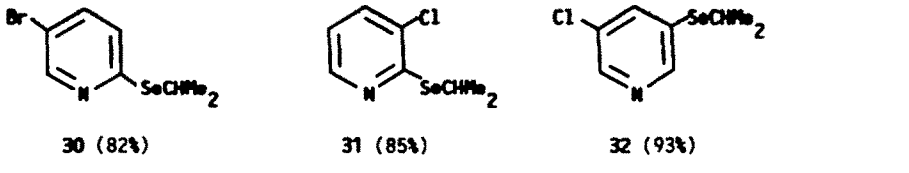
25 (71%)

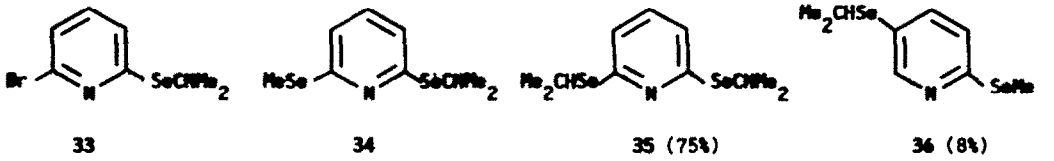
Only the syntheses of the 2-, 3-, and 4-phenylselenenylpyridines are reported in the literature; these however are not so straightforward as those described in this paper. Thus, compound **10** was obtained from the reaction of dimethyl 4-chloropyridine-2,6-dicarboxylate with benzeneselenol, followed by hydrolysis and decarboxylation.[19] Compounds **8** and **9** were prepared from **1** and **2** by substitution with PhSeNa in ethanol at 120 °C (sealed tube) using bis(bipyridine)nickel dibromide as a catalyst.[20] Finally, compound **8** was also obtained from the photostimulated $S_{RN}1$ reaction of **1** with phenylselenolate anions in liquid ammonia.[21]

The reactions of the monohalogenopyridines **1** - **3** with MeSeLi (2 mol. equiv.) were carried out at 70 °C. Compounds **11** and **13** were obtained with the yields indicated in Scheme 1. In the case of the 3-bromopyridine, **2**, on the contrary, even at the early reaction stages the reaction product was the 3-pyridylselenolate anion **26** (Scheme 2), as demonstrated by nmr analysis of the reaction mixture after treatment with ethyl iodide. Complete transformation was obtained after 6 h.

SCHEME 2







Addition of EtI afforded 3-ethylselenenylpyridine, whereas addition of MeI afforded the desired 3-methylselenenylpyridine **12** (R = Me). In this case therefore the dealkylation of **12** to **26** by MeSeLi is a faster process than the substitution of **2** by MeSeLi to give **12** (Scheme 2). This behaviour is identical to that observed in the case of chlorobenzene and bromobenzene.[11] Dealkylation is not observed with **1** and **3** since the aromatic substitution is strongly activated when the halogen atoms occupy the 2 or 4 position of the pyridine nucleus; thus, even in the presence of an excess of MeSe anions, the only process which can occur in these cases is the unproductive replacement of the MeSe group by another MeSe group.

The monosubstitution reactions of the bishalogenopyridines **4** - **7** were carried out at room temperature with 2 mol. equiv. of MeSeLi; only in the case of **7** the substitution required higher reaction temperature (60 °C). The final reaction mixture was treated with MeI so that, if small amounts of dealkylation products were formed, these were reconverted into the methylselenenyl derivatives. As indicated in Scheme 1, the monosubstitution products were obtained in good yields. In this case also the reactions with **5** and **6** were completely regioselective.

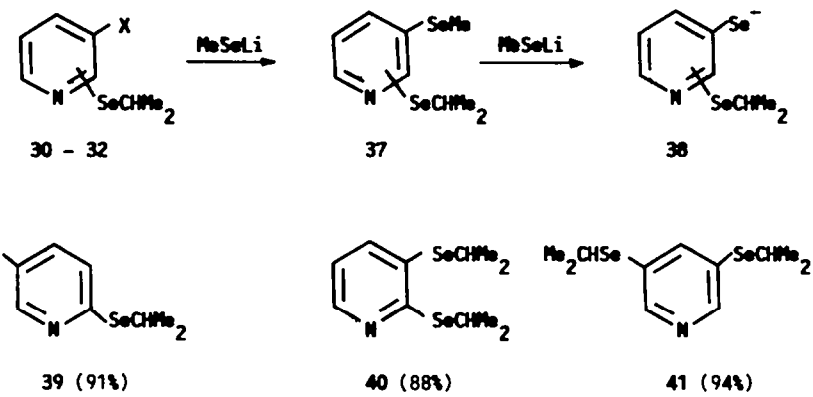
In order to effect the substitution of both the halogen atoms in **4** - **7** experiments were carried out with 4 mol. equiv. of MeSeLi at 80 °C. However, the initially formed monosubstitution products **18** - **21** (Scheme 2) rather than substitution to give compounds **27** suffered demethylation to afford the halogenopyridylselenolate anions **29**. Only in the case of **4**, in which both the bromine atoms are in the α positions, the reaction gave considerable amounts of the bissubstituted compound **27** which was present as the monodemethylated compound **28**. The same process occurred also in the case of **5**, but to a much lower extent. The reaction mixtures containing the selenolate anions were therefore treated with i-propyl iodide (see below); the results obtained are summarized in Scheme 2. From **5**, **6** and **7** good yields of the i-propylselenenyl halogenopyridines **30**, **31**, and **32**, respectively, were obtained. From the reaction of **5**, small amounts of a second reaction product were isolated. This was identified as the 2-methylselenenyl,5-i-propylselenenyl pyridine **36** deriving from **28**. The formation of this compound indicates that the dealkylation of the 2,5-bis(methylselenenyl)pyridine **27** occurs selectively at the MeSe group in the β position. In the light of the results obtained from the reactions of the monohalogenopyridines with MeSeLi (see above) this selective dealkylation is not completely unexpected. Nmr analysis of the reaction mixture deriving from **4** showed the presence of compounds **33** and **34**, deriving from **29** and **28**, respectively, in almost equimolecular amounts; the two products were not separated. The reaction of **4** was repeated using a large excess of MeSeLi (6 mol. equiv.) and longer reaction times (20 h) at 90 °C. After addition of Me_2CHI the 2,6-bis(i-propylselenenyl)pyridine **35** was isolated in 75 % yield. The formation of this compound is interesting since it indicates that under these conditions, complete substitution has occurred and that the 6-methylselenenyl,2-pyridylselenolate anion **28** has suffered further dealkylation to afford the dianion. This behaviour is peculiar since in all the poly(alkylthio)benzenes [8] and the bis(alkylselenenyl)benzenes [11] previously studied the S_N2 dealkylation process involves only one function; complete dealkylation occurs only by an electron transfer reaction [1,9,11] (see below) under completely different experimental conditions.

The behaviour of **5**, **6**, and **7** in the reactions with an excess of MeSeLi is similar to that observed in the case of the dichlorobenzenes;[11] in those cases also the monosubstituted products did not give further aromatic substitution but were instead dealkylated to the chlorophenyl selenolate anions. This similarity of behaviour is reasonable since in compounds **30**, **31** and **32** the halogeno atoms occupy a β position which is scarcely activated towards nucleophilic attack.

Thus, with the exception of **4**, starting from the dihalogenopyridines **5**, **6** and **7** and MeSeLi it

is not possible to introduce directly two selenium containing functions because in the methylselenenyl halogenopyridines 19 - 21 the demethylation is much faster than the nucleophilic substitution of the second halogen atom. This problem obviously does not exist when an arylselenolate anion is used as the nucleophile and it can be suggested that similar good results could be obtained with the use of alkylselenolate anions having secondary or tertiary alkyl groups. Unfortunately these selenolates are not so easily available as the MeSeLi. Thus, the synthesis of bis(alkylselenenyl)pyridines using MeSeLi were carried out stepwise. For this reason the halogenopyridylselenolate anions 29 were treated with i-propyl iodide and compounds 30 - 32 were thus obtained (Scheme 2). The presence of a secondary alkyl group should greatly decrease the rate of the S_N2 dealkylation process and the nucleophilic substitution should become the only observed process. Indeed, when the i-propylselenenyl halogenopyridines 30 - 32 (Scheme 3) were treated with excess MeSeLi (4 mol. equiv.) at 90 °C, the products obtained were the i-propylselenenyl pyridylselenolates 38 deriving from the easy demethylation of the substitution products 37. These anions can be directly treated with several alkylating agents. We added to the cooled reaction mixtures i-propyl iodide and the bis(i-propylselenenyl)pyridines 39 - 41 were thus obtained in good yields (Scheme 3).

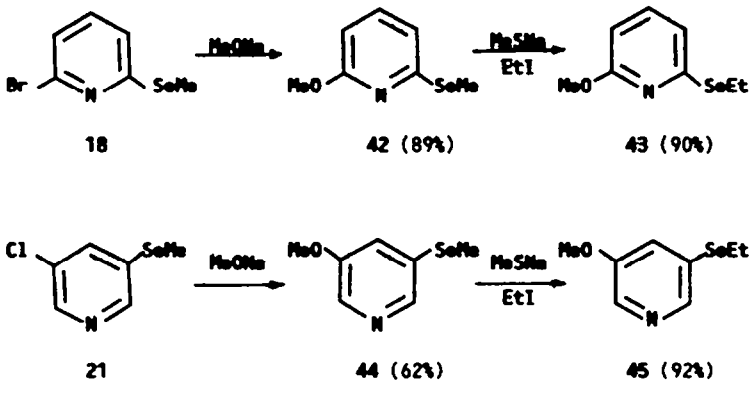
SCHEME 3



The monosubstituted compounds 18 - 21 were then used for the synthesis of the methoxy methylselenenylpyridines. For this purpose compounds 18 - 21 were treated with MeONa (2 mol. equiv.) in DMF at 80 °C for 4 h. The substitution process occurred easily with 18 and 21 (Scheme 4) to give 42 and 44, respectively. Complex reaction mixtures were instead obtained from 19 and 20. This behaviour is similar to that observed in the reactions of corresponding halogeno methylthiopyridines with MeONa in DMF;[18] thus, the reactions of 19 and 20 were not analyzed further.

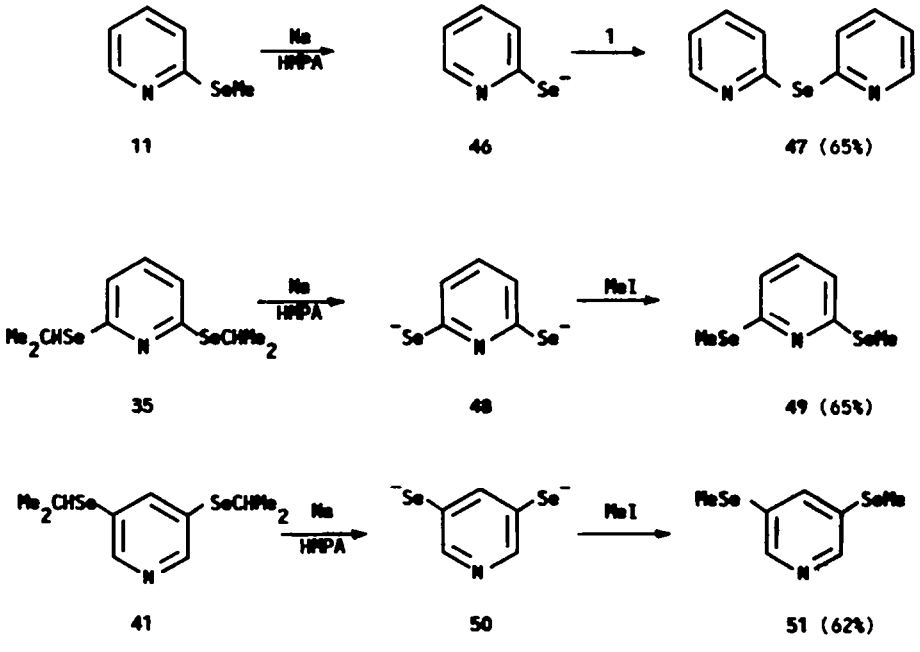
Experiments were also carried out to investigate the dealkylation of some of the obtained products. Compounds 42 and 44 were treated with MeSNa (4 mol) in DMF at 80 °C for 2 h. Ethyl iodide was then added to the resulting reaction mixtures. As indicated in Scheme 4 the sole reaction products were the 6-methoxy,2-ethylselenenylpyridine, 43, and the 5-methoxy,3-ethyl selenenylpyridine, 45, respectively. These results indicate that the dealkylation process is extremely selective and involves the SeMe group to give the methoxypyridylselenolate anions. Also in the case of the methoxyphenyl methyl selenides the S_N2 deakylation occurred selectively at the

SCHEME 4



SeMe group without touching the methoxy group.[11] Similar results were also obtained when 42 and 44 were dealkylated by electron transfer by treatment with excess sodium in HMPA[11] at 80 °C. This procedure was also applied to the 2-methylselenenylpyridine 11 and to the bis(i-propylselenenyl) pyridines 35 and 41 (Scheme 5); in these latter cases the dealkylation involved both the $SeCHMe_2$ groups. The 2-pyridylselenolate anion 46 was directly treated with 2-bromopyridine (2 mol. equiv.) at 120 °C for 4 h, and the bis(2-pyridyl)selenide 47 was obtained in 65% yield. The dianions 48 and 50 were instead treated with methyl iodide and the 2,6-bis(methylselenenyl)pyridine, 49, and the 3,5-bis(methylselenenyl)pyridine, 51, were thus obtained. The procedure here described for the preparation of the 2-pyridylselenolate anion 46 compares favourably with other methods described in the literature.[26,27]

SCHEME 5



In conclusion simple reaction conditions are described to introduce one or two phenylselenenyl groups into the pyridine nucleus by direct nucleophilic substitution of several halogeno pyridines. The corresponding reactions with methylselenolate anions lead in most cases to the pyridylselenolate anions deriving by the dealkylation of the initially formed substitution products; thus, in the case of the bis(halogeno)pyridines the introduction of two alkylselenenyl groups must be effected stepwise. No attempts were made to isolate the pyridylselenols by treating with acids the reaction mixtures containing the pyridylselenolate anions **26**, **46**, **29**, **38**, **48**, **50** and those deriving from the dealkylation of **42** and **44**. With the exception of **46** all the other pyridylselenolates were treated with simple alkyl iodides. However, there is no doubt that these solutions can be employed to synthesize other selenium containing pyridines simply by adding other electrophilic reagents, as it has already been done in the case of substituted phenylselenolate anions[11] as well as in the case of vinylselenolate anions.[28] Thus the addition of cyanogen halides, aryl halides, vinyl halides or acyl halides should give rise to the formation of pyridylselenocianates, pyridyl aryl selenides, pyridyl vinyl selenides or pyridyl acyl selenides; moreover, the addition of an oxidizing agent should produce the corresponding pyridyl diselenides. Thus, the syntheses of several selenium containing pyridines can be easily effected starting from selenium metal and an halogenopyridine according to the simple procedure described in this paper.

EXPERIMENTAL

Proton nmr spectra were recorded in $CDCl_3$ solutions on a 90 MHz Varian EM390 instrument. Glc analyses were performed on a Hewlett-Packard 5830A chromatograph with a 20 in., 10% UCW 982 column. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyzer. Commercial halogenopyridines were used without further purification.

Reactions of Halogenopyridines with Selenolate Anions.

Sodium phenylselenolate was prepared by adding sodium hydride to a stirred solution of diphenyldiselenide in DMF at 60 °C.

Lithium methyl selenide was prepared by adding dropwise methyllithium (commercial solution 1.6M in ether, 1.1 mol) to a stirred suspension of powdered gray selenium (1 atom) in THF (10 ml for 0.5 g of selenium) at room temperature and under nitrogen. After 15 min. all the selenium was consumed and a white suspension was obtained.

The reactions were carried out using 0.01 mol of halogenopyridine in the case of compounds **1** - **7** and 5 mmol in all the other cases. The molar equivalents of PhSeNa and MeSeLi, as well as the reaction temperatures, are reported under the Results and Discussion section.

A solution of the halogenopyridine in DMF was added to the suspension of PhSeNa or MeSeLi prepared as described above and the flask was immersed into a silicone oil bath kept at the desired temperature. The ether and the THF were left to distill off under vacuum. The resulting brown mixture was stirred for the times indicated below. The progress of the reaction was monitored by tlc, glc and/or nmr after treatment of small aliquots of the reaction mixture with ethyl iodide. The cooled reaction mixture was treated with the appropriate alkylating agent and then poured on water. Extraction with ether followed by the usual work up gave a residue which was chromatographed through a silica gel column by using mixtures of ethyl ether and petroleum ether as eluant. Reaction yields are given in parentheses in Schemes 1 - 5. The physical, nmr and

analytical data of the obtained products are reported below. Solid compounds (14 - 16 and 22, 23 and 25) were obtained in a pure form by evaporation of the chromatographic fractions and were not recrystallized. Starting materials and reactions times are indicated in parentheses in the order.

2-Phenylselenenylpyridine, 8, (1, 3 h), oil, (Lit.[20] b.p. 190 °C/0.1 mm). NMR δ 8.4 - 8.25 (m, 1 H); 7.75 - 7.5 (m, 2 H); 7.4 - 7.1 (m, 4 H); 7.0 - 6.8 (m, 2 H). Found: C = 56.76, H = 3.65, N = 6.20%. Requires: C = 56.42, H = 3.88, N = 5.98%.

3-Phenylselenenylpyridine, 9, (2, 20 h), oil, (Lit.[20] b.p. 190 °C/0.15 mm). NMR δ 8.75 - 8.55 (m, 1 H); 8.55 - 8.35 (m, 1 H); 7.75 - 7.55 (m, 1 H); 7.55 - 7.35 (m, 2 H); 7.35 - 7.0 (m, 4 H). Found: C = 56.21, H = 3.71, N = 5.85%. Requires: C = 56.42, H = 3.88, N = 5.98%.

4-Phenylselenenylpyridine, 10, (3, 2 h), oil, (Lit.[19] b.p. 143 - 145 °C/1.5 mm). NMR δ 8.4 - 8.2 (m, 2 H); 7.7 - 7.5 (m, 2 H); 7.5 - 7.2 (m, 3 H); 7.2 - 7.0 (m, 2 H). Found: C = 56.59, H = 3.77, N = 5.87%. Requires: C = 56.42, H = 3.88, N = 5.98%.

2-Methylselenenylpyridine, 11, (1, 5 h), oil, (Lit.[22] b.p. 43 - 44 °C/0.25 mm). NMR δ 8.4 (ddd, 1 H, J = 1.2, 1.8 and 5.1 Hz); 7.4 (ddd, 1 H, J = 1.8, 6.6 and 7.8 Hz); 7.2 (ddd, 1 H, J = 1.2, 1.8 and 7.8 Hz); 6.95 (ddd, 1 H, J = 1.8, 5.1 and 6.6 Hz); 2.45 (s, 3 H). Found: C = 41.94, H = 4.03, N = 8.26%. Requires: C = 41.87, H = 4.11, N = 8.14%.

3-Methylselenenylpyridine, 12, (2, 6 h), oil. NMR δ 8.7 - 8.55 (m, 1 H); 8.45 - 8.3 (m, 1 H); 7.7 (ddd, 1 H, J = 1.8, 2.4 and 7.8 Hz); 7.1 (ddd, 1 H, J = 0.6, 4.8 and 7.8 Hz); 2.35 (s, 3 H). Found: C = 41.66, H = 4.19, N = 8.25%. Requires: C = 41.87, H = 4.11, N = 8.14%.

3-Ethylselenenylpyridine, (2, 6 h), oil. NMR δ 8.7 - 8.55 (m, 1 H); 8.45 - 8.3 (m, 1 H); 7.8 (ddd, 1 H, J = 1.8, 2.4 and 7.8 Hz); 7.2 (ddd, 1 H, J = 0.6, 4.8 and 7.8 Hz); 2.95 (q, 2 H, J = 7.0 Hz); 1.45 (t, 3 H, J = 7.0 Hz). Found: C = 45.30, H = 4.79, N = 7.41%. Requires: C = 45.17, H = 4.87, N = 7.53%.

4-Methylselenenylpyridine, 13, (3, 2 h), oil.[23] NMR δ 8.4 - 8.25 (m, 2 H); 7.3 - 7.1 (m, 2 H); 2.35 (s, 3 H). Found: C = 41.95, H = 4.22, N = 8.04%. Requires: C = 41.87, H = 4.11, N = 8.14%.

2-Phenylselenenyl,6-bromopyridine, 14, (4, 1 h), m.p. 65 - 67 °C. NMR δ 7.8 - 7.6 (m, 2 H); 7.5 - 7.3 (m, 3 H); 7.3 - 7.15 (m, 2 H); 6.95 - 6.75 (m, 1 H). Found: C = 42.08, H = 2.70, N = 4.40%. Requires: C = 42.20, H = 2.58, N = 4.47%.

2-Phenylselenenyl,5-bromopyridine, 15, (5, 2 h), m.p. 52 - 54 °C. NMR δ 8.45 (dd, 1 H, J = 0.6 and 2.1 Hz); 7.8 - 7.55 (m, 2 H); 7.55 - 7.3 (m, 4 H); 6.9 (dd, 1 H, J = 0.6 and 7.8 Hz). Found: C = 42.31, H = 2.67, N = 4.40%. Requires: C = 42.20, H = 2.58, N = 4.47%.

2-Phenylselenenyl,3-chloropyridine, 16, (6, 5 h), m.p. 35 - 37 °C. NMR δ 8.2 (dd, 1 H, J = 1.5 and 4.8 Hz); 7.8 - 7.5 (m, 2 H); 7.5 - 7.15 (m, 4 H); 6.95 (dd, J = 4.8 and 8.1 Hz). Found: C = 49.31, H = 3.13, N = 5.10%. Requires: C = 49.19, H = 3.00, N = 5.21%.

3-Phenylselenenyl,5-chloropyridine, 17, (7, 15 h), oil. NMR δ 8.45 (d, 1 H, J = 1.8 Hz); 8.4 (d, 1 H, J = 2.1 Hz); 7.65 (dd, 1 H, J = 1.8 and 2.1 Hz); 7.6 - 7.45 (m, 2 H); 7.45 - 7.2 (m, 3 H). Found: C = 49.06, H = 2.88, N = 5.28%. Requires: C = 49.19, H = 3.00, N = 5.21%.

2-Methylselenenyl,6-bromopyridine, 18, (4, 1 h), oil. NMR δ 7.4 - 7.1 (m, 1 H); 2.45 (s, 1 H). Found: C = 28.63, H = 2.32, N = 5.70%. Requires: C = 28.71, H = 2.41, N = 5.58%.

2-Methylselenenyl,5-bromopyridine, 19, (5, 5 h), oil. NMR δ 8.5 (dd, 1 H, J = 0.9 and 2.4 Hz); 7.5 (dd, 1 H, J = 2.4 and 8.4 Hz); 7.2 (dd, 1 H, J = 0.9 and 8.4 Hz); 2.45 (s, 3 H). Found: C = 28.60, H = 2.49, N = 5.47%. Requires: C = 28.71, H = 2.41, N = 5.58%.

2-Methylselenenyl,3-chloropyridine, 20, (6, 3 h), oil. NMR δ 8.35 (dd, 1 H, J = 1.5 and 4.5 Hz); 7.45 (dd, 1 H, J = 1.5 and 7.8 Hz); 6.9 (dd, 1 H, J = 4.5 and 7.8 Hz); 2.45 (s, 3 H). Found: C = 34.95, H = 2.85, N = 6.87%. Requires: C = 34.89, H = 2.93, N = 6.78%.

3-Methylselenenyl,5-chloropyridine, 21, (7, 5 h), oil. NMR δ 8.5 (d, 1 H, J = 1.8 Hz); 8.35 (d, 1 H J = 1.8 Hz); 7.7 (t, 1 H, J = 1.8 Hz); 2.45 (s, 3 H); Found: C = 34.80, H = 2.82, N = 6.69%. Requires: C = 34.89, H = 2.93, N = 6.78%.

2,6-Bis(phenylselenenyl)pyridine, 22, (4, 20 h), m.p. 120 - 122 °C. NMR δ 7.75 - 7.5 (m, 4 H); 7.5 - 7.15 (m, 6 H); 7.05 (t, 1 H, J = 7.5 Hz); 6.65 (d, 2 H, J = 7.5 Hz). Found: C = 52.40, H = 3.30, N = 3.71%. Requires: C = 52.45, H = 3.37, N = 3.60%.

2,5-Bis(phenylselenenyl)pyridine, 23, (5, 15 h), m.p. 52 - 54 °C. NMR δ 8.45 (dd, 1 H, J = 0.6 and 2.1 Hz); 7.75 - 7.55 (m, 2 H); 7.55 - 7.1 (m, 9 H); 6.85 (dd, 1 H, J = 0.6 and 7.8 Hz). Found: C = 52.40, H = 3.45, N = 3.75%. Requires: C = 52.45, H = 3.37, N = 3.60%.

2,3-Bis(phenylselenenyl)pyridine, 24, (6, 20 h), oil. NMR δ 8.15 (dd, 1 H, J = 1.8 and 4.5 Hz); 7.7 - 7.1 (m, 11 H); 6.75 (dd, 1 H, J = 4.5 and 7.8 Hz). Found: C = 52.38, H = 3.29, N = 3.51%. Requires: C = 52.45, H = 3.37, N = 3.60%.

3,5-Bis(phenylselenenyl)pyridine, 25, (7, 6 h), m.p. 54 - 56 °C. NMR δ 8.45br (s, 2 H); 7.75 - 7.6 (m, 1 H); 7.5 - 7.35 (m, 4 H); 7.35 - 7.1 (m, 6 H). Found: C = 52.39, H = 3.26, N = 3.69%. Requires: C = 52.45, H = 3.37, N = 3.60%.

2-i-Propylselenenyl,5-bromopyridine, 30, (19, 1 h), oil. NMR δ 8.5 (d, 1 H, J = 2.4 Hz); 7.5 (dd, 1 H, J = 2.4 and 8.4 Hz); 7.2 (d, 1 H, J = 8.4 Hz); 4.0 (spt, 1 H, J = 7.0 Hz); 1.55 (d, 6 H, J = 7.0 Hz). Found: C = 34.49, H = 3.55, N = 5.10%. Requires: C = 34.44, H = 3.61, N = 5.02%.

2-i-Propylselenenyl,3-chloropyridine, 31, (20, 4 h), oil. NMR δ 8.35 (dd, 1 H, J = 1.5 and 4.8 Hz); 7.5 (dd, 1 H, J = 1.5 and 7.8 Hz); 6.95 (dd, 1 H, J = 4.8 and 7.8 Hz); 4.1 (spt, 1 H, J = 7.0 Hz); 1.6 (d, 6 H, J = 7.0 Hz); Found: C = 40.85, H = 4.30, N = 5.89%. Requires: C = 40.96, H = 4.30, N = 5.97%.

3-i-Propylselenenyl,5-chloropyridine, 32, (21, 6 h), oil. NMR δ 8.55 (d, 1 H, J = 1.8 Hz); 8.45

(d, 1 H, J = 2.1 Hz); 7.85 (dd, 1 H, J = 1.8 and 2.1 Hz); 3.5 (spt, 1 H, J = 7.0 Hz); 1.45 (d, 6 H, J = 7.0 Hz). Found: C = 41.30, H = 4.42, N = 5.78%. Requires: C = 40.96, H = 4.30, N = 5.97%.

2-Methylselenenyl,5-i-propylselenenylpyridine, 36, oil. NMR δ 8.6 (dd, 1 H, J = 0.9 and 2.4 Hz); 7.6 (dd, 1 H, J = 2.4 and 8.4 Hz); 7.2 (dd, 1 H, J = 0.9 and 8.4 Hz); 3.35 (spt, 1 H, J = 7.0 Hz); 2.5 (s, 3 H); 1.4 (d, 6 H, J = 7.0 Hz). Found: C = 36.98; H = 4.60; N = 4.96%. Requires: C = 36.87, H = 4.48, N = 4.78%.

2,6-Bis(i-propylselenenyl)pyridine, 35, (4, 15 h), oil. NMR δ 7.2 - 6.9 (m, 3 H); 4.05 (spt, 2 H, J = 7.0 Hz); 1.55 (d, 12 H, J = 7.0 Hz). Found: C = 41.27, H = 5.50, N = 4.15%. Requires: C = 41.14, H = 5.33, N = 4.36%.

2,5-Bis(i-propylselenenyl)pyridine, 39, (30, 6 h), oil. NMR δ 8.6 (d, 1 H, J = 2.4 Hz); 7.6 (dd, 1 H, J = 2.4 and 8.4 Hz); 7.2 (d, 1 H, J = 8.4 Hz); 4.0 (spt, 1 H, J = 7.0 Hz); 3.35 (spt, 1 H, J = 7.0 Hz); 1.55 (d, 6 H, J = 7.0 Hz); 1.4 (d, 6 H, J = 7.0 Hz). Found: C = 41.00, H = 5.13, N = 4.53%. Requires: C = 41.14, H = 5.33, N = 4.36%.

2,3-Bis(i-propylselenenyl)pyridine, 40, (31, 20 h), oil. NMR δ 8.35 (dd, 1 H, J = 1.8 and 4.5 Hz); 7.65 (dd, 1 H, J = 1.8 and 7.5 Hz); 6.9 (dd, 1 H, J = 4.5 and 7.5 Hz); 4.0 (spt, 1 H, J = 7.0 Hz); 3.6 (spt, 1 H, J = 7.0 Hz); 1.6 (d, 6 H, J = 7.0 Hz); 1.45 (d, 6 H, J = 7.0 Hz). Found: C = 41.25, H = 5.12, N = 4.29%. Requires: C = 41.14, H = 5.33, N = 4.36%.

3,5-Bis(i-propylselenenyl)pyridine, 41, (32, 20 h), oil. NMR δ 8.65 (d, 2 H, J = 1.8 Hz); 8.05 (t, 1 H, J = 1.8 Hz); 3.5 (spt, 2 H, J = 7.0 Hz); 1.45 (d, 12 H, J = 7.0 Hz). Found: C = 41.03, H = 5.14; N = 4.48%. Requires: C = 41.14, H = 5.33, N = 4.36%.

The reactions with sodium methoxide were carried out and worked up as described above for the reactions with the selenolate anions.

2-Methylselenenyl,6-methoxypyridine, 42, (18, 4 h) oil. NMR δ 7.3 (dd, 1 H, J = 7.2 and 7.8 Hz); 6.85 (dd, 1 H, J = 0.9 and 7.2 Hz); 6.45 (dd, 1 H, J = 0.9 and 7.8 Hz); 3.95 (s, 3 H); 2.45 (s, 3 H). Found C = 41.65, H = 4.40, N = 6.99%. Requires: C = 41.59, H = 4.50, N = 6.93%.

3-Methylselenenyl,5-methoxypyridine, 44, (21, 4 h), oil. NMR δ 8.2 (d, 1 H, J = 1.8 Hz); 8.1 (d, 1 H, J = 2.7 Hz); 7.2 (dd, 1 H, J = 1.8 and 2.7 Hz); 3.85 (s, 3 H); 2.4 (s, 3 H). Found: C = 41.68, H = 4.43, N = 6.81%. Requires: C = 41.59, H = 4.50, N = 6.93%.

Dealkylation Reactions with Sodium Methanethiolate.

The mixture of the methoxypyridyl methyl selenide (5 mmol) and commercial MeSNa (20 mmol) in DMF (15 ml) was kept at 80 °C for 2 h. The cooled reaction mixture was treated with ethyl iodide and then worked up in the usual way. Reaction yields are reported in Scheme 4.

2-Ethylselenenyl,6-methoxypyridine, 43, (42, 2 h), oil. NMR δ 7.35 (t, 1 H, J = 6.9 Hz); 6.9 (d, 1 H, J = 6.9 Hz); 6.45 (d, 1 H, J = 6.9 Hz); 4.0 (s, 3 H); 3.2 (q, 2 H, J = 7.0 Hz); 1.55 (t, 3 H, J

= 7.0 Hz). Found: C = 44.60, H = 5.22, N = 6.40%. Requires: C = 44.45, H = 5.14, N = 6.48%.

3-Ethylselenenyl,5-methoxypyridine, 45, (**44**, 2 h), oil. NMR δ 8.3 (d, 1 H, J = 1.8 Hz); 8.15 (d, 1 H, J = 2.7 Hz); 7.3 (dd, 1 H, J = 1.8 and 2.7 Hz); 3.85 (s, 3 H); 2.95 (q, 2 H, J = 7.0 Hz); 1.45 (t, 3 H, J = 7.0 Hz). Found: C = 44.54, H = 5.06, N = 6.53%. Requires: C = 44.45, H = 5.14, N = 6.48%.

Dealkylation Reactions with Sodium.

To a solution of the alkylselenenylpyridine (5 mmol) in HMPA (10 ml), stirred under nitrogen at 100 °C, small pieces of sodium (2 equiv. for each SeR group) were added. The progress of the reaction was monitored by tlc, glc and/or nmr after treatment of small aliquots of the reaction mixture with ethyl iodide. In the case of **11**, 2-bromopyridine (10 mmol) was added and the resulting mixture was stirred at 120 °C for 4 h. On the contrary, in the case of **35** and **41** the reaction mixture was cooled and methyl iodide was added. The mixture was worked up and the product was isolated in the usual way. Reaction yields are reported in Scheme 5.

Bis(2-pyridyl)selenide, 47, oil.[21] NMR δ 8.55 - 8.45 (m, 1 H); 7.6 - 7.45 (m, 2 H); 7.2 - 7.0 (m, 1 H). Found: C = 51.14, H = 3.52, N = 11.85%. Requires: C = 51.07, H = 3.43, N = 11.91%.

2,6-Bis(methylselenenyl)pyridine, 49, (**35**, 2 h), oil. NMR δ 7.2 - 6.9 (m, 1 H); 2.5 (s, 2 H). Found: C = 31.83, H = 3.54, N = 5.39%. Requires: C = 31.72, H = 3.42, N = 5.28%.

3,5-Bis(methylselenenyl)pyridine, 51, (**41**, 2 h), oil. NMR δ 8.45 (d, 2 H, J = 1.8 Hz); 7.8 (t, 1 H, J = 1.8 Hz); 2.4 (s, 6 H). Found: C = 31.79, H = 3.31, N = 5.35%. Requires: C = 31.72, H = 3.42, N = 5.28%.

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