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DIRECT PHOSPHORYLATION OF BENZOTHIAZOLES AND 4-METHYLTHIAZOLE

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Abstract: Simple procedures for preparation of 2-(4-methylthiazolyl) dichlorophosphine and wide variety of 2-phosphorylated benzothiazoles are reported. Efficient promoters and catalysts were found for the key transformation, direct phosphorylation of the heterocyclic compounds by PCl_3 (PBr_3 as a promoter) or by P(V) acid chlorides ($HgCl_2$ as a catalyst).

1,3-Azoles undergo smooth C-phosphorylation by phosphorus(III) halides[1] and by P(V) acid chlorides[2]. Direct C(2)-phosphorylation of thiazoles and benzothiazoles is not known, however. The only analogous reaction described in the literature is C(5)-phosphorylation of 2-amino-methinethiazoles[3]. There are a few examples of indirect approaches to benzothiazol-2-yl-substituted phosphines[4], none of which is satisfactory in terms of yield and/or simplicity of synthetic procedure.

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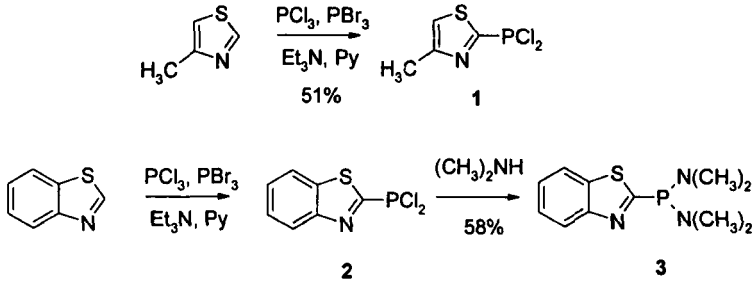
Benzothiazolyl- and thiazolyldihalophosphines, as well as benzothiazolyl-substituted phosphinic and phosphonic acids, which would be of great preparative and biological interest, have not been reported to date. We now report simple procedures for direct C(2)-phosphorylation of benzothiazoles and 4-methylthiazole, both by P(III) halides and P(V) acid chlorides.

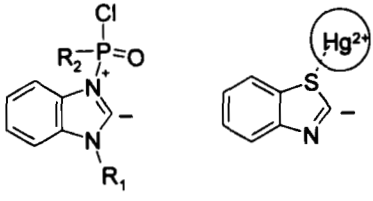
C(2)-Phosphorylation of benzothiazole and 4-methylthiazole by an excess of PCl_3 in pyridine-triethylamine proceeds smoothly if a promoter - PBr_3 - is added to the reaction mixture. Noteworthy, PCl_3 alone does not react, while the action of the too-reactive PBr_3 leads to substantially diminished yield of the C-phosphorylated product. The dichlorophosphines **1, 2** can be isolated in moderate yield and characterized. Benzothiazol-2-yldichlorophosphine was transformed into the corresponding amidophosphinite **3** (scheme 1):



Scheme 1

When benzothiazole was treated with P(V) acid chlorides ($PhPOCl_2$ or CH_3POCl_2) in Py-NEt_3, only the starting material was recovered. This was in marked contrast with N-substituted benzoimidazoles, the efficient reaction of which with P(V) acid chlorides was described previously[2]. We suggested that metal ions or complexes able to coordinate to benzothiazole could activate the heterocyclic ring for this reaction, which was postulated to proceed through ylide intermediates in case of benzoimidazoles[2,5] (structure **A** in Fig.1). Analogous structures **B** could be intermediates in case of benzothiazoles.

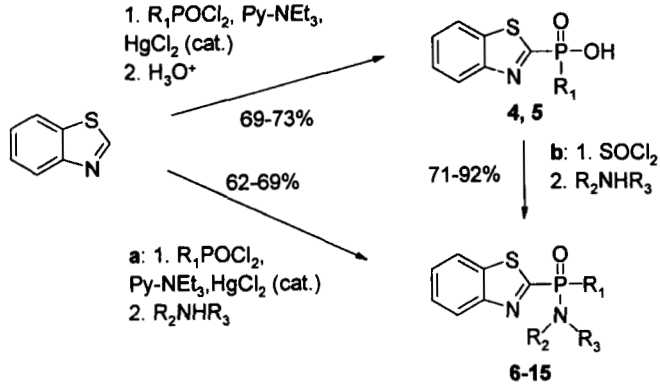
Actually, catalytic amounts of Hg^{2+} salts promoted the reaction and after the work-up corresponding phosphinic acids or



A B

Fig. 1

their amides were isolated in good yield. The best results were achieved with $HgCl_2$. Optimal conditions were found in a series of experiments in an NMR sample tube by monitoring the C(2)-H ^{1}H-NMR signal. Py-d_5 was used as a solvent, the amount of catalyst ($HgCl_2$) was varied. An approximately 1:10 molar ratio of catalyst-benzothiazole gave the maximum yield. Larger amounts of $HgCl_2$ diminish the yield presumably due to strong coordination of Hg^{2+} with the final product, especially with benzothiazolyl-substituted phosphinic acids or their salts. The corresponding phosphinic acids **4, 5** were conveniently obtained directly from the reaction mixture. Amides **6-15** can also be synthesized directly (path **a**), or from the purified acids (path **b**, scheme 2).



4, $R_1 = CH_3$

5, $R_1 = Ph$

6, $R_1 = CH_3$, $R_2+R_3 = (CH_2)_5$

7, R_1=Ph,$R_2+R_3 = (CH_2)_2O(CH_2)_2$

8, $R_1 = Ph$, $R_2 = R_3 = Et$

9, R_1=Ph, R_2+R_3=$(CH_2)_5$

10, $R_1 = Ph$, $R_2+R_3 = (CH_2)_6$

11, $R_1 = CH_3$, $R_2+R_3 = (CH_2)_2O(CH_2)_2$

12,R_1=Ph,R_2+R_3=$(CH_2)_2N(CH_3)(CH_2)_2$

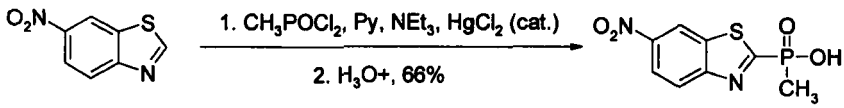
13, R_1=Ph, R_2=H, R_3=$(CH_2)_2Ph$

14, R_1=Ph, R_2=H, R_3=2-FC_6H_4

15, R_1=Ph,R_2 = H, R_3 =1,3-thiazol-2-yl

Scheme 2

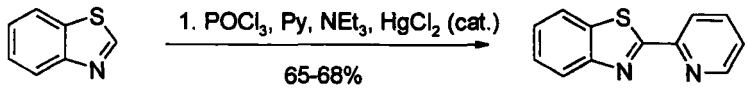
It is of interest to perform C-phosphorylation of nitrobenzothiazoles which would open the way to other phosphorylated benzothiazole derivatives. Direct phosphorylation of nitro-substituted heterocycles by P(III) halophosphines is impossible, because of oxidation reactions involving the nitro group[6]. Reaction of P(V) acid chlorides with nitrobenzoimidazoles was shown to proceed without problems[2]. 6-Nitrobenzothiazole also reacts with CH_3POCl_2 in Py-NEt_3 mixture, in the presence of a catalytic amount of $HgCl_2$. In this case, the reaction is slower compared to the unsubstituted benzothiazole, which could be due to the diminished nucleophilicity of the ylide intermediate. Acid **16** was isolated (scheme 3).



16

Scheme 3

Reaction of benzothiazole with $POCl_3$ under the conditions described above led unexpectedly not to the C-phosphorylated product. Instead, compound **17** was formed (scheme 4):



17

Scheme 4

The structure of the main product of the reaction was confirmed by comparison of its spectroscopic and analytical data with those for **17** synthesized by a known procedure[7]. We have reported an oxidative coupling of N-alkylbenzoimidazoles[2] where the corresponding bis-benzoimidazolyles were formed, but benzothiazole has coupled with the solvent - pyridine. As in the case of benzoimidazole, this reaction could be an alternative preparative approach to **17**.

EXPERIMENTAL

NMR spectra were recorded on a Bruker WP-100SY spectrometer (100.13 MHz for protons), TMS was used as an internal standard for ^{1}H and ^{13}C-NMR spectra, 85% H_3PO_4 was an external standard for ^{31}P-NMR measurements. Melting points were measured on a hot stage and are uncorrected. Pyridine and triethylamine were dried over KOH and distilled.

4-Methyl-1,3-thiazol-2-yldichlorophosphine (1). Triethylamine (40 mmol), PCl_3 (33.4 mmol), and PBr_3 (6.6 mmol) were added in succession to a stirred solution of 4-methylthiazole (20 mmol) in pyridine (15 ml) at ambient temperature. The mixture was left to stand for 24 h. The solvent was distilled off in vacuum, the residue was dissolved in benzene (30 ml) and filtered. After removal of benzene, the product was distilled (66-70°C/0.05 mm). Pale yellow liquid (50.8% yield), ^{31}P-NMR (C_6D_6, d): 132.8; ^{1}H-NMR (C_6D_6 , d): 6.56 (1H, s, 5-H), 2.16 (3H, s, CH_3). ^{13}C-NMR (C_6D_6 , d): 169.8 (d, J_{P-H}=61.1 Hz, 2-C), 156.5 (d, J_{P-H}=14.4 Hz, 4-C), 121.2 (d, J_{P-H}=9.0 Hz, 5-C), 16.6 (CH_3).

1,3-Benzothiazol-2-yldichlorophosphine (2) was obtained analogously to **1**. Dichlorophosphine **2** decomposes slowly in solutions and by melting. Analytically pure **2** can be obtained by vacuum distillation (130-132°C/0.05 mm) in 20.4% yield. Pale yellow solid, m.p. 59-60°C (decomp.). ^{31}P-NMR (C_6D_6, d): 131.8; ^{1}H-NMR (C_6D_6 , d): 7.95 (1H, d, J=7.9 Hz, 4-H), 7.26 (1H, d, J=7.9 Hz, 7-H), 7.04 (1H, t, J=7.5 Hz, 6-H), 6.94 (1H, t, J=7.5 Hz, 5-H); ^{13}C-NMR (C_6D_6 , d): 172.7 (J_{P-H}=63.5 Hz, 2-C), 154.7 (J_{P-H}=16.1 Hz, 9-C), 137.4 (J_{P-H}=2.2 Hz, 8-C), 127.0 (5-C), 126.8 (6-C), 124.8 (4-C), 121.9 (7-C).

1,3-Benzothiazol-2-yl-N,N,N'N'-tetramethylphosphonous diamide (3). Crude **2** was dissolved in a minimal amount of toluene. Dimethylamine (a 6-fold excess) was added cautiously to the solution at -15°C under stirring. After being kept for 1 h at ambient temperature, the reaction mixture was filtered, the solvent was evaporated. Vacuum distillation of the residue gave yellow oil (119-121°C/0.05 mm) in 58.4% yield. ^{31}P-NMR (C_6D_6, d): 91.2; ^{1}H-NMR (C_6D_6 , d): 8.27 (1H, d, J=8.1 Hz, 4-H), 7.78 (1H, d, J=8.1 Hz, 7-H), 7.35 (1H, t, J=8.1 Hz, 6-H), 7.22 (1H, t, J=8.1 Hz, 5-

H), 2.87 (12H, d, J=9.6 Hz, CH_3); ^{13}C-NMR (C_6D_6 , d): 176.4 (d, J_{P-H}=8.15 Hz, 2-C), 156.6 (d, J_{P-H}=7.24 Hz, 9-C), 138.0 (s, 8-C), 125.7 (s, 5-C), 124.8 (s, 6-C), 123.5 (s, 4-C), 121.7 (s, 7-C), 42.1 (d, J_{P-H}=16.00 Hz, CH_3).

Phosphorylation of benzothiazole by $PhPOCl_2$ and CH_3POCl_2 was performed using the following standard procedure. To a stirred mixture of benzothiazole (1 equiv., usually 8 mmol), triethylamine (1.2 equiv., usually 9.6 mmol), $HgCl_2$ (0,1 equiv., usually 0.8 mmol) and pyridine (to obtain approximately 1 M solution of the heterocyclic compound) phosphorylating reagent (1.1 equiv.) in pyridine (1:1 vol.) was added dropwise during 10 min. The course of the reaction can be followed by ^{31}P-NMR spectroscopy. After no changes in the ^{31}P-NMR specta were observed, the reaction mixture was worked-up as described below.

1,3-Benzothiazol-2-yl(methyl)phosphinic acid (4) was obtained from benzothiazole (2.59 ml, 23.8 mmol) and $MePOCl_2$. The reaction mixture was poured carefully into a solution of sodium carbonate (102.5 mmol) in water (50 ml). Small amount of black tar was filtered off and the filtrate was evaporated. The residue was dissolved in 15 ml of water and the acid **4** was precipitated by addition of conc. HCl until pH=6, collected by filtration and dried *in vacuo* over P_4O_{10}. White crystals (from water), m.p. 123^{0}C (3.72 g, 73 %). ^{31}P-NMR (CD_3OD, d) 30; ^{1}*H*-NMR (CD_3OD, d) 8.18-7.95 (m, 2H), 7.60-7.37 (m, 2H), 1.76 (d, $^2J_{P-H}$=15.6Hz, 3H). ^{13}C-NMR (CD_3OD, d) 168.0 ($^1J_{C-P}$=104.8 Hz), 155.7 ($^3J_{C-P}$=15.4 Hz), 137.5, 129.3, 128.2, 125.1, 123.5, 15.7 ($^2J_{C-P}$=71.5 Hz). Anal. Calcd for $C_8H_8NO_2PS$: C, 45.07; H, 3.79; N, 6.57. Found: C, 44.95; H, 3.83; N, 6.63.

1,3-Benzothiazol-2-yl(phenyl)phoshpinic acid (5) was obtained from benzothiazole (1 ml, 9.17 mmol) and $PhPOCl_2$ analogously to **4**. Pale yellow powder, m.p. 99^{0}C (1.74 g, 69%). ^{31}P-NMR (CD_3OD, d) 19; ^{1}*H*-NMR (CD_3OD, d) 8.11-7.85 (m, 4H), 7.65-7.48 (m, 5H). Anal. Calcd for $C_{13}H_{10}NO_2PS$: C, 56.72; H, 3.66; N, 5.09. Found: C, 56.64; H, 3.72; N, 5.15.

1,3-Benzothiazol-2-yl(methyl)piperidinophosphine oxide (6) was obtained from benzothiazole (1.68 ml, 15.41 mmol) and CH_3POCl_2. After phosphorylation the reaction mixture was treated with piperidine (6.67 ml, 67.56 mmol). Than it was

evaporated to dryness, and the product was extracted with benzene. Ammonium salts were filtered off and the solvent was removed under reduced pressure. The oil remained was crystallized from heptane. Pale red crystalls, m.p. 71°C (2.66 g, 62%). ^{31}P-NMR ($CDCl_3$, d) 31; ^1H-NMR ($CDCl_3$, d) 8.29-7.92 (m, 2H), 7.67-7.33 (m, 2H), 3.33 (m, 4H), 1.95(d, $^2J_{H-H}$=15.4 Hz, 3H), 1.69-1.38 (m, 6H). Anal. Calcd for $C_{13}H_{17}N_2OPS$: C, 55.70; H, 6.12; N, 10.00. Found: C, 55.59; H, 6.16; N, 10.08.

1,3-Benzothiazol-2-yl(morpholino)phenylphosphine oxide (7) was obtained from benzothiazole (0.3 ml, 2.75 mmol) and $PhPOCl_2$. The reaction mixture was treated with morpholine (1.06 ml, 12.18 mmol). Than it was evaporated to dryness, and the product was extracted from the solid with benzene. Ammonium salts were filtered off and the solvent was removed. The product was chromatographed on silica gel Merck 60 with ethylacetate as an eluent to give **7**. Recrystallized from hexane, white crystals, m.p. 121°C (653 mg, 69%). ^{31}P-NMR ($CDCl_3$, d) 19; ^1H-NMR ($CDCl_3$, d) 8.38-7.88 (m, 4H), 7.67-7.38 (m, 5H), 3.72 (m, 4H), 3.22 (m, 4H). Anal. Calcd for $C_{17}H_{17}N_2O_2PS$: C, 59.29; H, 4.98; N, 8.14. Found: C, 59.14; H, 5.02; N, 8.22.

1,3-Benzothiazol-2-yl-N,N-diethyl(phenyl)phosphinic amide (8) was obtained from benzothiazole (1.5 ml, 13.80 mmol) and $PhPOCl_2$. After phosphorylation the reaction mixture was treated with diethylamine (6.24 ml, 0.121 mol), evaporated, and the product was extracted from the remained solid with benzene. Ammonium salts were filtered off and the solvent was removed under reduced pressure. The product was chromatographed on silica gel Merck 60, ethylacetate-benzene 2:1 as an eluent to give **8**. Recrystallized from hexane, white crystals, m.p. 81°C (2.87 g, 63%). ^{31}P-NMR ($CDCl_3$, d) 20; ^1H-NMR (CD_3OD, d) 8.13-7.70 (m, 4H), 7.57-7.31 (m, 5H), 3.06 (m, 4H), 0.93 (t, 6H). Anal. Calcd for $C_{17}H_{19}N_2OPS$: C, 61.80; H, 5.80; N, 8.48. Found: C, 61.74; H, 5.83; N, 8.51.

Synthesis of amides 9-16 from phosphinic acids 4,5. Corresponding phosphinic acid (1 equiv.) was refluxed with an exess of thionyl chloride for 6 h. $SOCl_2$ was evaporated in vacuum and the residue was dissolved in dry 1,4-dioxane. A solution of the appropriate secondary amine (3.5 equiv.) or primary amine (1 equiv.) and

triethylamine (2.5 equiv.) in 1,4-dioxane was added dropwise to the stirred solution of the acid choride during 5 min. The mixture was stirred for about 30 min. The work-up is described below.

1,3-Benzothiazol-2-yl(phenyl)piperidinophosphine oxide (9) was obtained from acid **5** (690 mg, 2.51 mmol) and piperidine. The reaction mixture was diluted with 5-fold exess of 5% aq. K_2CO_3 and the product was collected by filtration. Colorless crystalls, m.p. 116°C (704 mg, 82%). ^1H-NMR ($CDCl_3$, d) 8.32-7.89 (m, 4H), 7.67-7.32 (m, 5H), 3.32-2.98 (m, 4H), 1.78-1.42 (m, 6H). Anal. Calcd for $C_{18}H_{19}N_2OPS$: C, 63.14; H, 5.59; N, 8.18. Found: C, 63.02; H, 5.64; N, 8.23.

1-Azepanyl(1,3-benzothiazol-2-yl)phenylphosphine oxide (10) was obtained from acid **5** (690 mg, 2.51 mmol) and azepane analogously to **9**. Yellow crystalls, m.p. 112°C (769 mg, 86%).^1H-NMR ($CDCl_3$, d) 8.33-7.92 (m, 4H), 7.71-7.35 (m, 5H), 3.42-3.08 (m, 4H), 1.79-1.48 (m, 8H). Anal. Calcd for $C_{19}H_{21}N_2OPS$: C, 64.03; H, 5.94; N, 7.86. Found: C, 63.96; H, 5.98; N, 7.93.

1,3-Benzothiazol-2-yl(methyl)morpholinophosphine oxide (11) was obtained from acid **4** (670 mg, 3.14 mmol) and morpholine. After the reaction the mixture was evaporated *in vacuo* and the residue was crystallised from water. Colorless crystalls, m.p 145°C (691 mg, 78%). ^1H-NMR ($CDCl_3$, d) 8.30-7.91 (m, 2H), 7.72-7.42 (m, 2H), 3.67 (t, 4H, J=5.5 Hz), 3.47-2.98 (m, 4H), 1.99 (d, $^2J_{P\text{-}H}$=15.0 Hz, 3H). Anal. Calcd for $C_{12}H_{15}N_2O_2PS$: C, 51.06; H, 5.36; N, 9.92. Found: C, 50.99; H, 5.40; N, 9.98.

1,3-Benzothiazol-2-yl(4-methylpiperazino)phenylphosphine oxide (12) was obtained from acid **5** (660 mg, 2.40 mmol) and 1-methylpiperazine. The reaction mixture was evaporated *in vacuo* and dissolved in 15 ml of 5% aq. K_2CO_3. The product was extracted by ether (3x30 ml), washed by water, dried ($MgSO_4$) and the solvent was evaporated. The residue was dried *in vacuo*. Pale yellow solid, m.p.134°C (695 mg, 81%). ^1H-NMR ($CDCl_3$, d) 8.33-7.91 (m, 4H), 7.69-7.37 (m, 5H), 3.42-3.11 (m, 4H), 2.43 (t, 4H, J=6 Hz), 2.29 (s, 3H). Anal.Calcd for $C_{18}H_{20}N_3OPS$: C, 60.49; H, 5.64; N, 11.76. Found: C, 60.35; H, 5.72; N, 11.85.

1,3-Benzothiazol-2-yl-N-phenethyl(phenyl)phosphinic amide (13) was obtained from acid **5** (690 mg, 2.51 mmol) and phenethylamine analogously to **9**. Pale

yellow crystalls, m.p. 127°C (874 mg, 92%). ^1H-NMR ($CDCl_3$, d) 8.31-7.85 (m, 4H), 7.67-7.43 (m, 6H), 7.35-7.06 (m, 5H), 3.33 (m, 2H), 2.90 (t, 2H, J=5.8 Hz). Anal. Calc for $C_{21}H_{19}N_2OPS$: C,66.65;H, 5.06; N, 7.40. Found: C,66.52; H,5.11;N, 7.48.

1,3-Benzothiazol-2-yl-N-(2-fluorophenyl)phenylphosphinic amide (14) was obtained from acid **5** (690 mg, 2.51 mmol) and o-fluoroaniline and triethylamine. Colorless solid, m.p. 158°C (703 mg, 76%). ^1H-NMR ($CDCl_3$, d) 8.36-7.88 (m, 4H), 7.72-7.32 (m, 6H), 7.20-7.03 (m, 1H), 7.00-6.81 (m, 2H), 6.76 (d, 1H, J=8 Hz). Anal. Calcd for $C_{19}H_{14}FN_2OPS$: C, 61.95; H, 3.83; N, 7.60. Found: C, 61.83; H, 3.88; N, 7.55.

1,3-Benzothiazol-2-yl)(phenyl)-N-(1,3-thiazol-2-yl)phosphinic amide (15) was obtained from acid **5** (810 mg, 2.95 mmol), 1,3-thiazol-2-amine and triethylamine. After reaction the mixture was diluted with 5-fold exess of 5% aq. K_2CO_3 and the product was collected by filtration, washed by water and ether and dried in vacuum. Yellow solid, m.p. 185°C (749 mg, 71%). ^1H-NMR ($CDCl_3$/DMSO-D_6, d) 8.19-7.85 (m, 4H), 7.63-7.33 (m, 5H), 6.94 (d, 1H, J=4.2 Hz), 6.46 (d, 1H, J=4.2 Hz). Anal. Calcd for $C_{16}H_{12}N_3OPS_2$: C, 53.77; H, 3.38; N, 11.76. Found: C, 53.84; H, 3.42; N, 11.84.

Methyl(6-nitro-1,3-benzothiazol-2-yl)phosphinic acid (16). CH_3POCl_2 (1.55 ml, 10.9 mmol) was added carefully to a stirred mixture of 6-nitro-1,3-benzothiazole (10,9 mmol), NEt_3 (2.08 ml, 15 mmol), pyridine (15 ml) and $HgCl_2$ (300 mg) under dry nitrogen atmosphere. The formed solution was then left to stand at 40°C for about 8 days, carefully poured into an aqueous solution of K_2CO_3 (20%, 50 ml). The precipitate was filtered off, the filtrate was acidified to pH~ 2. Crystals of **16** were filtered and dried (66% yield). ^{31}P-NMR (CD_3OD, d): 11; ^{1}H-NMR (CD_3OD, d): 8.63 (d, ^4J=2 Hz, 1H), 8.24 (dd, ^3J=8.5 Hz, ^4J=2 Hz, 1H) 7.80-8.05 (m, 2H), 7.69 (d, ^3J=8.5 Hz, 1H), 7.30-7.60 (m, 3H), 4.74 (q, 2H), 1.28 (t, 3H). Anal. Calcd for $C_8H_7N_2O_4PS$: C, 37.22; H, 2.73, N, 10.85 Found: C, 37.15; H, 2.78, N, 10.88

2-(2-Pyridyl)-1,3-benzothiazole (17). A mixture of benzothiazole (1 equiv.), pyridine (to get about 10% soln. of benzothiazole), triethylamine (3.5 equiv.), $HgCl_2$

(0.1 equiv.) was treated with $POCl_3$ (1.1 equiv.), and the mixture was allowed to stand overnight. Then it was carefully poured into 10% solution of potassium carbonate, and the product was extracted with CH_2Cl_2, washed with water, dried, evaporated. Vacuum distillation gave **17**, in 65-68% yield, all spectral characteristics of which correspond to that of the authentic sample[7].

LITERATURE AND NOTES

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