PERKIN 1
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Preparation and reactions of 2-pyridyltellurium derivatives

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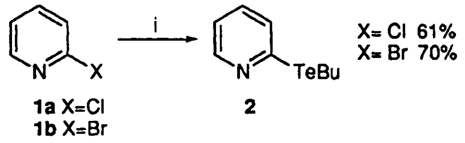
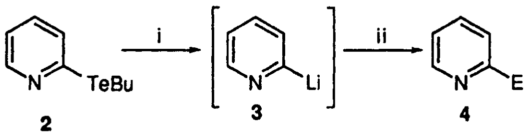
Pyridyltellurium derivatives have been prepared from the reaction of halopyridines with lithium butanetellurolate and the tellurium–metal exchange of pyridyltellurium derivatives has been investigated using butyllithium and dilithium dimethylcyanocuprate.

Synthetic applications of organotellurium compounds have increased in recent years.[1] Among their many synthetic uses, transmetallations with organolithium or organocuprate reagents are considered to be important for carbon–carbon bond formation.[2] In connection with our recent studies on pyridylmetal derivatives,[3] we have investigated the preparation and reactions of 2-pyridyltellurium compounds. Butyl 2-pyridyl telluride was prepared by the nucleophilic substitution of 2-bromopyridine and 2-chloropyridine with lithium butanetellurolate to give the telluride **2** in 70% and 61% yields, respectively.



Scheme 1 *Reagents and conditions:* i, BuTeLi, reflux, 92 h

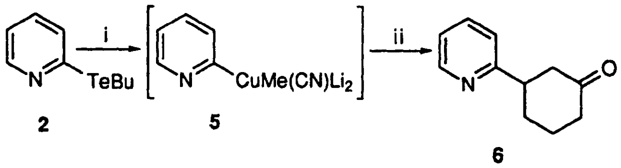
Tellurium–metal exchange was then investigated using butyllithium. Compound **2** was treated with butyllithium in THF at −78 °C and then benzaldehyde, to give phenyl-(2-pyridyl)methanol (73%). Other electrophiles, namely methyl *N*-methylbenzohydroxamate or 1,2-diiodoethane reacted to give 2-benzoylpyridine and 2-iodopyridine in 64% and 50% yields, respectively. From those results, the tellurium–lithium exchange is considered to proceed smoothly to form 2-pyridyllithium.



electrophile	E	Yield (%)
PhCHO	CH(OH)Ph	73
PhCONMeOMe	COPh	64
ICH_2CH_2I	I	50

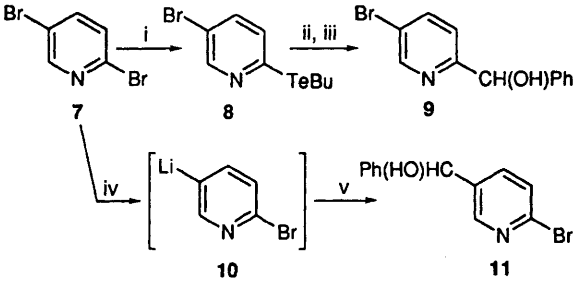
Scheme 2 *Reagents and conditions:* i, BuLi, THF, −78 °C; ii, electrophile, RT

Transmetallation with dilithium dimethylcyanocuprate[4] was also examined. Compound **2** was treated with dilithium dimethylcyanocuprate in THF at −20 °C for 1.5 h, and cyclohex-2-enone was added. The 1,4-addition proceeded to give 3-(2-pyridyl)cyclohexanone **6** (41%).



Scheme 3 *Reagents and conditions:* i, $Me_2Cu(CN)Li_2$, THF, −20 °C, 1.5 h; ii, cyclohex-2-enone (41%)

2,5-Dibromopyridine **7** is known to be lithiated at the 5-position on reaction with butyllithium[5] and we confirmed this by trapping the 2-bromo-5-lithiopyridine **10** with benzaldehyde to form 2-bromo-5-[phenyl(hydroxy)methyl]pyridine **11**. In order to develop a new pathway for 2-lithio-5-bromopyridine, we prepared butyl 5-bromo-2-pyridyl telluride **8**, which was prepared using the same method as for the preparation of **2** and examined the tellurium–lithium exchange of **8**. The telluride **8** was treated with butyllithium in THF at −78 °C followed by the addition of benzaldehyde to give 5-bromo-2-[phenyl-(hydroxy)methyl]pyridine **9**.



Scheme 4 *Reagents and conditions:* i, BuTeLi, THF, RT (55%); ii, BuLi, THF, −78 °C; iii, PhCHO (70%); iv, BuLi, THF, −100 °C; v, PhCHO, RT (62%)

Pyridyltellurium derivatives are readily accessible by the nucleophilic substitution of halopyridines with lithium butanetellurolate, and this method is applicable to some extent at other positions of the pyridine ring. Further application of pyridyltellurium derivatives in synthetic chemistry is under investigation.

Experimental

Butyl 2-pyridyl telluride 2

Under an Ar atmosphere, tellurium powder (273 mg, 214 mmol) was suspended in dry THF (8 ml) and a solution of BuLi in THF (1.39 mol dm^{-3}; 1.5 ml, 2.09 mmol) was added to the mixture, which was stirred for 10 min. The mixture was cooled to −78 °C and 2-bromopyridine (317 mg, 2.01 mmol) was added at that temperature. The mixture was then allowed to warm to ambient temperature and then refluxed for 92 h. After completion of the reaction, the mixture was diluted with H_2O (50 ml) and the aqueous mixture was extracted with

Et_2O (50 ml × 3). The ethereal extracts were dried ($MgSO_4$) and evaporated and the residue was purified by column chromatography on SiO_2 using hexane–AcOEt (4:1) as eluent. The crude material was distilled under reduced pressure to give a viscous oil (368 mg, 70%): δ_H(300 MHz; $CDCl_3$) 0.93 (3 H, t, *J* 7.3), 1.43 (2 H, sextet, *J* 7.3), 1.89 (2 H, quintet, *J* 7.5), 3.12 (2 H, t, *J* 7.5), 7.00–7.03 (1 H, m), 7.28–7.34 (1 H, m), 7.47 (1 H, dd, *J* 2.0 and 7.7), 8.47 (1 H, dd, *J* 1.1 and 4.0); *m*/*z* 265 (M^+) (Found: M^+, 265.0111. Calc. for $C_9H_{13}NTe$ *M*, 265.0111).

General procedure for the generation of 2-lithiopyridine

Under an Ar atmosphere, a solution of BuLi in THF (1.35 mol dm^{-3}, 0.60 ml, 0.81 mmol) was added dropwise to a mixture of **2** (210 mg, 0.80 mmol) and dry THF (10 ml) at −78 °C. The mixture was stirred for 5 min followed by the addition of an electrophile (see Scheme 2). The mixture was allowed to warm gradually to room temperature and stirred for 20 h (44 h for 2-iodopyridine). The usual work-up gave a 2-substituted pyridine.

References

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Paper 6/02767I
Received 22*nd April* 1996
Accepted 7*th June* 1996