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NOVEL SYNTHESIS OF 3-HALOGENOBENZO[b]TELLUROPHENE-DERIVATIVES*

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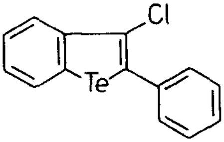
Summary: Several substituted benzo[b]tellurophenes were prepared from phenylacetylenes and TeO_2 in the presence of a lithium halide, LiX.

Since the first synthesis of benzo[b]tellurophene in 1971,[1] a number of 2- and 3-functionalized derivatives has been synthesized by multi-step procedures.[2,3] The only halogen-substituted derivative described so far in the literature is 3-chloro-2-phenylbenzo[b]tellurophene[4] (1), obtained from the 1:1 adduct of $TeCl_4$ and diphenylacetylene[5] (2a) by heating (214°C) in trichlorobenzene. On the other hand, attempts to cyclize the corresponding 1:1 adduct between $TeCl_4$ and phenylacetylene[5] (2b), has been unsuccessful.[6]



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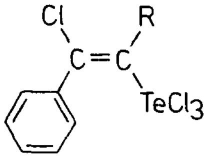
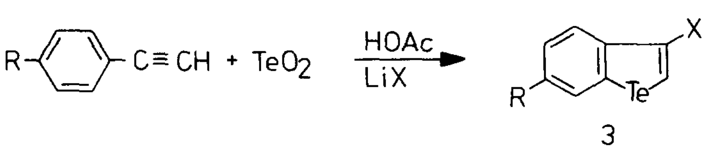


2

a R= C_6H_5
b R= H

In this paper we report a one-step synthesis of 3-halogeno-substituted benzo[b]tellurophene derivatives with TeO_2 as the tellurium source.



3

a R= H , X= Cl
b R= H , X= Br
c R= H , X= I
d R= CH_3 , X= Cl
e R= Br , X= Cl

When treated with BuLi even at -100° in ether 3b is easily ring-opened. Such reactions are well-documented in the selenophene series,[7] and the selenium isologue of 4 has been obtained[8]

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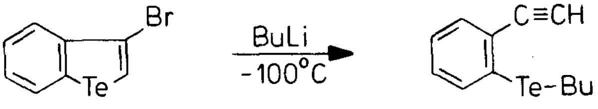
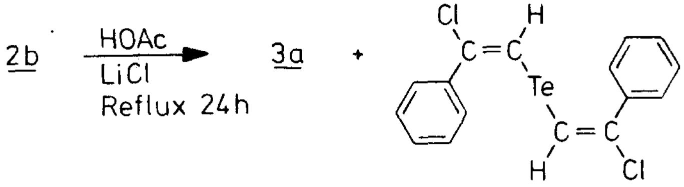
* Part 3 in the series "Tellurium in Organic Syntheses". For part 2, see ref. 9.

similarly.

In order further to prove the structure of 3a and to cast some light upon its formation, 2b was treated with HOAc/LiCl at reflux. When LiCl is omitted only 5 is formed.



3b 4



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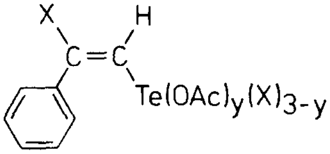
In an earlier paper[9] we have described the acetoxymethylation of some aromatic compounds with TeO_2/HOAc in the presence of LiBr. In these reactions TeO_2 serves merely as an oxidizing agent for acetic acid. In the present case TeO_2, dissolved by interaction with LiX, adds to the triple bond rather than attacking the solvent. We have tentatively assigned structure (6) to the primary product which cyclizes to the benzo[b]tellurophene derivative (7), probably by loss of HOAc (cf the high reactivity of $Hg(OAc)_2$ as compared with $HgCl_2$ against aromatics).[10] The last step in the reaction sequence should be a reductive elimination yielding compounds of type 3.



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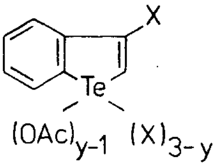

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