SYNTHESIS OF BENZOTELLUROPHENE DERIVATIVES

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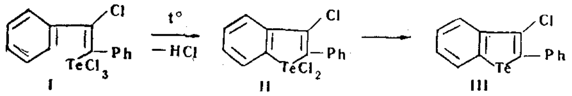
A number of methods for the synthesis of benzothiophene [1] and benzoselenophene derivatives are known. However, benzotellurophene derivatives have still not been obtained, although a method for the synthesis of tellurophene was recently proposed [2]. Although it is true that the literature does contain a reference [3] to the preparation of 3-telluronaphthenol, it was not subsequently confirmed and, considering the extreme instability of sulfur and, particularly, selenium analogs [4] of this compound, is doubtful.

The usual synthetic methods used in the benzothiophene and benzoselenophene series cannot be extended to benzotellurophene because of the peculiarity of the chemical behavior of derivatives of tellurium. We have shown that the synthesis of benzotellurophene derivatives can be accomplished by means of smooth cyclization of the product (I) [5] of the addition of tellurium tetrachloride to diphenylacetylene.



The cyclization product, 1,1,3-trichloro-2-phenylbenzotellurophene (II), is converted almost quantitatively to 3-chloro-2-phenylbenzotellurophene (III) by the action of sodium sulfide. The method proposed for the preparation of III is similar to the method for the synthesis of 2-phenyl-3-chlorobenzoselenophene from selenium tetrachloride and diphenylacetylene [6], but intermediate products I and II cannot be isolated in the latter case.

The IR spectrum of III contains bands at 1600 and 1580 cm^{-1} (benzene ring) and at 770-690 cm^{-1} which are characteristic for the out-of-plane deformation vibrations of mono- and o-disubstituted benzene, while the NMR spectrum (concentrated CCl_4 solution) contains only signals from the aromatic protons. The electronic absorption spectrum of the final product is almost identical to the spectrum of 2-phenyl-3-chlorobenzoselenophene, which confirms structure III.

EXPERIMENTAL

1,1,3-Trichloro-2-phenylbenzotellurophene (II). A mixture of 25 g of 2-chloro-1,2-diphenylvinyltellurium trichloride and 25 ml of 1,2,4-trichlorobenzene was refluxed until HCl evolution ceased (2-2.5 h). The hot solution was filtered off from a small amount of tellurium metal and cooled. The precipitate was filtered and washed with petroleum ether to give 11.76 g (51.2%) of II, which, by crystallization from toluene (with charcoal), gives gold-yellow plates with mp 247-248°. Found %: Te 30.8; Cl 25.8. $C_{14}H_9Cl_3Te$. Calc. %: Te 31.0; Cl 25.9.

2-Phenyl-3-chlorobenzotellurophene (III). II [6.5 g (15 mmole)] was mixed thoroughly with 19 g (79 mmole) of $Na_2S \cdot 9H_2O$, and the mixture was heated at 100-110° for 20 min. The crude product was filtered, washed with water, and dried in a vacuum desiccator to give 5.1 g (95%) of light-yellow crystals of III with mp 102-103° (from propanol). Found %: Te 37.5. $C_{14}H_9ClTe$. Calc. %: Te 37.5.

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