SYMMETRIZATION OF CYCLIC σ-TELLURANES

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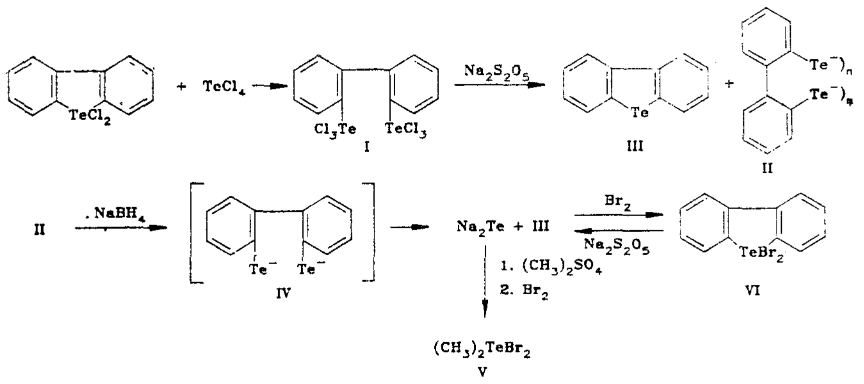
We have previously reported [1] the symmetrization of noncyclic σ-telluranes Ar_2TeCl_2 upon treatment with tellurium tetrachloride, leading to σ-telluranes of the type $ArTeCl_3$. Similar reactions involving cyclic σ-telluranes are unknown.

We have now demonstrated that refluxing 5,5-dichlorodibenzotellurophene with tellurium tetrachloride in o-dichlorobenzene results in symmetrization and the formation of 2,2'-bis-(trichlorotelluro)diphenyl (I) in high yield; the latter compound has not been described previously. Reduction of this compound with aqueous sodium metabisulfite gives, in addition to the polymeric ditelluride II, contaminated with metallic tellurium, dibenzotellurophene (III) in 8% yield. The latter is also formed in high yield (91%) upon reduction of ditelluride II with sodium borohydride in ethanol, apparently as a result of disproportionation of the intermediate ditellurolate anion IV to sodium telluride and dibenzotellurophene. In fact, workup of the reaction mixture with dimethyl sulfate, followed by bromination and separation of the product mixture based on their widely different solubilities, leads to dimethyltellurium dibromide (V) and 5,5-dibromodibenzotellurophene (VI), which was isolated in the form of dibenzotellurophene (III) by reductinn of VI with $Na_2S_2O_5$.



The disproportionation of dianion IV is similar to the decomposition of the ditellurolate anion, obtained via reduction of poly(methylene)ditelluride, to sodium telluride and poly(methylene)telluride [2].

2,2'-Bis(trichlorotelluro)diphenyl (I). Yellow-gold crystals, mp 250°C (dec., from o-dichlorobenzene); 87% yield.

Ditelluride (II). Black powder, insoluble in organic solvents.

Dibenzotellurophene (III). Yellow needles, mp 96°C (from hexane) (according to [3], mp 95°C).

Dimethyltellurium Dibromide (V). Colorless plates, mp 95°C (from ethanol) (according to [4], mp 94-95°C).

Elemental analyses of compounds I, III, and V were consistent with calculated values.

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CONCERNING THE RECYCLIZATION OF PYRROLO[2,1-a]ISOQUINOLINES TO BENZ[g]INDOLES

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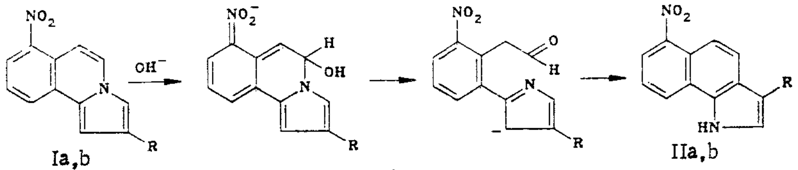
Indolizines containing a nitro group in the pyridine ring are capable of isomerizing upon treatment with base under mild conditions to give the corresponding nitroindoles [1]. An analogous rearrangement, although requiring harsher conditions, has also been demonstrated to occur for quaternary isoquinolinium salts containing a methyl or methylene group in the α-position relative to the heteroatom in the ring [2].

Based on these reactions, one would assume that a pyrrolo[2,1-a]isoquinoline molecule, which contains both an indolizine as well as an isoquinoline fragment, should also be capable of recyclization upon treatment with base. In order to answer this question, we have synthesized a series of pyrrolo[2,1-a]isoquinolines, among them some with a nitro group in the benzene portion of the molecule.

Our experiments have revealed that both the unsubstituted pyrroloisoquinoline, as well as pyrroloisoquinolines with methyl and phenyl substituents in the 2-position, exhibit high stability with respect to reactions with nucleophilic reagents.

Introduction of a nitro group to the benzene portion of the pyrroloisoquinoline would be expected to increase the sensitivity of the system to reactions with nucleophiles and thus confer more favorable conditions for recyclization. In fact, upon heating in aqueous ethanolic base solution, both 2-methyl-7-nitro- and 2-phenyl-7-nitropyrrolo[2,1-a]isoquinoline (Ia, b) isomerized in the absence of oxygen to give the corresponding benz[g]indoles (IIa, b) in high yields:



I–IIa R=CH_3; b R=C_6H_5

3-Methyl-6-nitrobenz[g]indole (IIa). This was prepared by refluxing a mixture of 50 mg of compound Ia, 4 g KOH, 2 ml water, and 18 ml ethanol for 3 h in a inert gas stream. The resulting crystals of IIa were separated and washed with water. Yield 88%, mp 240-242°C (dec., from toluene). PMR spectrum ($CDCl_3$): 3.3 (s, 3H, CH_3), 4.7 (s, 1H, NH), 8.8-9.6 ppm (m, 6H, aromatic protons). IR spectrum: 3075-3150 (NH), 1360 ($\nu_{NO_2}{}^{s}$), 1515 cm^{-1} ($\nu_{NO}{}^{as}$).

6-Nitro-3-phenylbenz[g]indole (IIb). This was prepared under analogous conditions by refluxing for 10 h. Yield 84%, mp 265-266°C (dec., from toluene). PMR spectrum ($CDCl_3$): 4.4 (s, 1H, NH), 8.9-9.8 ppm (m, 11H, aromatic protons). IR spectrum: 3080-3400 (NH), 1360 ($\nu_{NO_2}{}^{s}$), 1520 ($\nu_{NO_2}{}^{as}$), 3000-3100 cm^{-1} (C–H).

Elemental analyses of compounds IIa, b were consistent with calculated values.

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