Synthesis of dimercaptoarsenic iodides

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Introduction: The new $^{72}Se/^{72}As$-solid-phase-extraction-generator-system [1] and the As-Ge-seperation (described in [2]) deliver nca AsI_3. The subsequent step for the future labelling of biomolecules with radioactive arsenic isotopes is to synthesize a small precursor molecule based on AsI_3.
The basic idea of this work is to inhibit 2 binding sites of the arsenic in oxidation state +III with a very stable compound while one binding site remains for coupling to a biomolecule, e.g. via nucleophilic substitution.
As arsenic-sulphur bonds are most stable, this work describes the coupling of AsI_3 with different dimercapto-compounds.

Experimental:
General procedure for the synthesis of dimercapto-arsenic iodides:
147,90 mg AsI_3 (0.325 mmol) are dissolved in 5 ml anhydrous dichloromethane via ultrasound. The mixture is stirred under argon, cooled down with liquid nitrogen and protected against light with aluminium foil. An equimolar amount of a dimercapto-compound and 51.3 µl pyridine (0.65 mmol) are carefully added. The mixture is then allowed to warm up and stirred for 1 hour at room temperature. Formed pyridinium-salts are removed via filtration. FD-MS is performed directly with this solution. To isolate the solid yellow products, argon is blown carefully over the solution to remove the solvent. With storage in CH_2Cl_2 solution at T= -18°C under argon the compounds are stable for about 1 month.

The following dimercaptanes have been used:
- 1,3-dimercaptopropan (1)
- 1,2-dimercaptopropanol (2)
- 2,3-dimercaptobutan (3)
- 1,3-dimercaptobenzol (4)
- 1,2-dimercaptobenzol (5)
- 2,3-dimercaptoamberic acid (6)

Results and Discussion: The reaction scheme showed in Fig.1 indicates that the reaction is sensible to polymerisation. To prevent this, it is necessary to work oxygen- and light-free at low temperatures. Nevertheless, four of the tested six mercaptanes tended to polymerize (Fig.2).

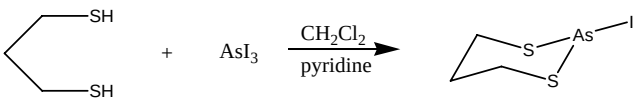

Fig.1: Exemplary scheme for the reaction of dimercaptanes with arsenic triiodide

Table of the used reactants and their products

Reactant	MM (product)	FD-MS	Yield [%]	Properties
1	308.06	307.8	> 90	yellow powder, stable in solution at T= -18 °C for 1 month
2	324.05	-	-	polymerisation
3	322,07	321.8	40	Yellow, instable, many side-products, polymerisation
4	342.07	341.8	>90	yellow powder, stable in solution at T= -18 °C for 2 days
5	342.07	-	-	polymerisation
6	382.05	-	-	polymerisation

It is consistent with literature that As is more stable in six- ring-configuration [4] and indeed, only 1,3-dimercaptopropan and 1,3-dimercaptobenzol gave products, which could be analyzed.

Until now, it has not been possible to obtain NMR-spectra of the dimercaptoarsenic iodides because it is not possible to exchange the solvent without polymerisation. However, the existence of the 1,3-dimercaptopropylarsenic iodide has been shown by FD-MS as well as by derivatisation to 1,3-dimercaptopropyl-mercaptoethyl arsenic (FD-MS: 242.9) and 1,3-dimercaptopropyl-1-hydroxyl-2-mercapto propyl arsenic (FD-MS: 272.8).

Conclusion: The synthesis and short-time stability of dimercaptoarsenic iodides could be shown and the influence of different dimercaptanes was demonstrated.
Six-rings formed from dimercaptanes with arsenic showed up to be more stable then five-rings.
1,3-dimercaptopropan gave best yields and will be the optimal precursor for future coupling reactions to biomolecules [1].

References:
[1] Jennewein, M. et al., Annual Report 2003
[2] Jennewein, M. et al., Annual Report 2002
[4] Holleman, Wiberg, Lehrbuch der anorg. Chem., 100th ed., 1985