

Improved Synthesis of CsN₃

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Dedicated to Professor Joachim Strähle on the Occasion of his 65th Birthday

Abstract. Cesium azide can conveniently be prepared from anhydrous CsF and (CH₃)₃SiN₃ in SO₂ solvent in high purity and yield. In this reaction, the initially generated SO₂F[−] anion is converted

in SO₂ solvent to solvated azide, (SO₂)_nN₃[−], which is labile and releases SO₂ under dynamic vacuum yielding pure CsN₃.

Keywords: Cesium azide; Fluorosulfite; Azidosulfite

Verbesserte Synthese von CsN₃

Inhaltsübersicht. Caesiumazid kann bequem durch die Reaktion von wasserfreiem CsF und (CH₃)₃SiN₃ in SO₂-Lösung in hoher Reinheit und Ausbeute dargestellt werden. In dieser Reaktion wird

das zuerst gebildete SO₂F[−]-Anion in SO₂-Lösung zu dem solvatisierten Azid, (SO₂)_nN₃[−] umgesetzt, das im dynamischen Vakuum labil ist und unter SO₂-Verlust reines CsN₃ ergibt.

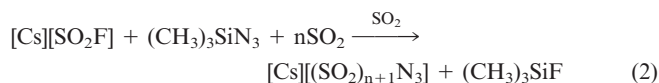
Sodium azide is a widely used reagent and is technically prepared from NaNH₂ and N₂O [1]. The heavier alkali metal azides are generally prepared starting from NaN₃. Two general methodologies for the preparation of heavier alkali metal azides such as CsN₃ have been employed. The most common preparative route utilizes an aqueous solution of HN₃ which is neutralized by the corresponding alkali metal hydroxide or carbonate [2–4]. Aqueous HN₃ is generally prepared from NaN₃ and H₂SO₄ [2]. In the second approach, cesium and rubidium azide have been prepared via ion exchange chromatography starting from aqueous NaN₃ [5]. Since the handling of HN₃ is potentially hazardous, a facile synthetic route to CsN₃ without the use of HN₃ is highly desirable. Circumventing the use of HN₃ and laborious chromatographic techniques, [N(CH₃)₄][N₃] has been prepared from [N(CH₃)₄][F] and (CH₃)₃SiN₃ in CH₃CN solvent [6]. In the present note, we present a new facile laboratory preparation of CsN₃ starting from (CH₃)₃SiN₃ and CsF in SO₂ solvent.

Results and Discussion

In analogy to the synthesis of [N(CH₃)₄][N₃], the preparation of CsN₃ was attempted from anhydrous CsF and excess (CH₃)₃SiN₃ in refluxing CH₃CN solvent. The reaction in CH₃CN solvent was found to be slow and did not yield pure CsN₃ even after five days. The reaction of CsF with neat (CH₃)₃SiN₃ was also found to be slow; even after three days at temperatures close to the boiling point of (CH₃)₃SiN₃ (93 °C) significant amounts of CsF were still

present. The sluggishness of these reactions is presumably a consequence of the insufficient solubility of CsF in CH₃CN and (CH₃)₃SiN₃. The removal of (CH₃)₃SiF and addition of fresh (CH₃)₃SiN₃ did not result in a significantly faster conversion, indicating either the absence of an equilibrium reaction or a coating of the starting material by the product.

Anhydrous CsF reacts with SO₂ solvent to the fluorosulfite anion, SO₂F[−] (eq. (1)) [7]. The reaction of [Cs][SO₂F] suspended in SO₂ with excess (CH₃)₃SiN₃ results in complete azide-fluoride exchange within less than one hour yielding a clear, yellow solution of [Cs][(SO₂)_nN₃] according to eq. (2).



Removal of the volatiles (SO₂ and (CH₃)₃SiF) at ambient temperature results in precipitation of yellow [Cs][(SO₂)₂N₃] which is converted to [Cs][SO₂N₃] and [Cs][N₃] upon prolonged pumping [8,9]. Pure [Cs][N₃] is obtained after SO₂ removal under dynamic vacuum at 55 °C yielding a white solid. Since [Cs][SO₂F] does not lose SO₂ at 55 °C, the complete conversion of F[−] to N₃[−] can be verified by the absence of signals associated with the SO₂F[−] anion in the Raman spectrum.

Experimental

Materials and Apparatus. All volatile materials were handled in a Pyrex vacuum line equipped with Kontes Teflon valves. Nonvolatile materials were handled in the dry argon atmosphere of a dry box. The solvents, CH₃CN (Baker) and SO₂ (Aldrich, >99.9%) were dried over P₄O₁₀ and CaH₂ and were freshly distilled prior to use. The CsF (KBI) was fused in a platinum crucible, transferred while hot to the dry box, and finely powdered. Trimethylsilyl azide (Ald-

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rich, 95%) was purified by fractional condensation through cold traps held at -35 and -196 °C and using the -196 °C fraction.

Preparation of CsN_3 . In a typical reaction, anhydrous CsF (2.952 g, 0.0194 mol) was suspended in 8.861 g SO_2 at room temperature inside a glass vessel equipped with a Kontes valve. Excess trimethylsilyl azide (2.754 g, 0.0239 mol) was condensed onto the frozen reaction mixture at -196 °C. Upon warming to room temperature, the solid phase turned yellow and dissolved in the liquid SO_2 within 40 min, yielding a two-phase system consisting of a lower yellow and an upper colorless layer. Volatiles were removed under dynamic vacuum at ambient temperatures for approximately 30 min, yielding a yellow solid. Further pumping at 50 to 55 °C for ca. 2 hours yielded pure, colorless $[\text{Cs}][\text{N}_3]$ (3.4 g; 0.0194 mol).

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