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Karl Christe (ERC), et al., "Improved Synthesis of CsN₃"

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(Statement A)

Improved Synthesis of CsN₃

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Received

Dedicated to Professor Joachim Straehle 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. Cäsiumazid kann bequem durch die Reaktion of 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⁻, konvertiert, welches im dynamischen Vakuum labil ist und unter SO₂ Verlust reines CsN₃ liefert.

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Introduction

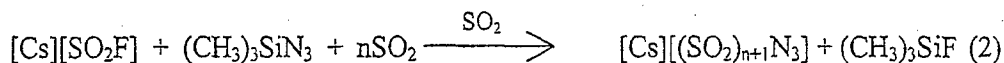
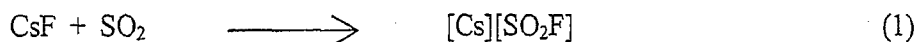
Sodium azide is a widely used reagent and is technically prepared from NaNH_2 and N_2O [1]. The heavier alkali metal azides are generally prepared starting from NaN_3 . Two general methodologies for the preparation of heavier alkali metal azides such as CsN_3 have been employed. The most common preparative route utilizes an aqueous solution of HN_3 which is neutralized by the corresponding alkali metal hydroxide or carbonate [2-4]. Aqueous HN_3 is generally prepared from NaN_3 and H_2SO_4 [2]. In the second approach, cesium and rubidium azide have been prepared via ion exchange chromatography starting from aqueous NaN_3 [5]. Since the handling of HN_3 is potentially hazardous, a facile synthetic route to CsN_3 without the use of HN_3 is highly desirable. Circumventing the use of HN_3 and laborious chromatographic techniques, $[\text{N}(\text{CH}_3)_4][\text{N}_3]$ has been prepared from $[\text{N}(\text{CH}_3)_4][\text{F}]$ and $(\text{CH}_3)_3\text{SiN}_3$ in CH_3CN solvent [6]. In the present note, we present a new facile laboratory preparation of CsN_3 starting from $(\text{CH}_3)_3\text{SiN}_3$ and CsF in SO_2 solvent.

Results and Discussion

In analogy to the synthesis of $[\text{N}(\text{CH}_3)_4][\text{N}_3]$, the preparation of CsN_3 was attempted from anhydrous CsF and excess $(\text{CH}_3)_3\text{SiN}_3$ in refluxing CH_3CN solvent. The reaction in CH_3CN solvent was found to be slow and did not yield pure CsN_3 even after five days. The reaction of CsF with neat $(\text{CH}_3)_3\text{SiN}_3$ was also found to be slow; even after three days at temperatures close to the boiling point of $(\text{CH}_3)_3\text{SiN}_3$ (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 CH_3CN and $(\text{CH}_3)_3\text{SiN}_3$. The removal of $(\text{CH}_3)_3\text{SiF}$ and addition of fresh $(\text{CH}_3)_3\text{SiN}_3$ 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. (2)) [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]. 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 SO₂F⁻ to N₃⁻ can be verified by the absence of signals associated with the SO₂F⁻ anion in the Raman spectrum.

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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

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

Preparation of CsN₃. In a typical reaction, anhydrous CsF (2.952 g, 0.0194 mol) was suspended in 8.861 g SO₂ 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 SO₂ 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 [Cs][N₃] (3.400 g; 0.0194 mol).

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