

Synthesis of Periodonaphthalene, C₁₀I₈: Permercuration and Subsequent Iododemercuration of Naphthalene in a Triiodide Solution

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ABSTRACT

Periodonaphthalene was synthesized in 12.6% yield by permercuration of naphthalene, followed by iododemercuration in a solution of potassium triiodide. MS and elemental analyses established the compound's identity and purity, respectively. We propose two potential applications for periodonaphthalene.

Key Words: Periodonaphthalene; Octaiodonaphthalene; Naphthalene; Permercuration; Iodination; Mass spectrometry; Calibration compound; Fullerenes.

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INTRODUCTION

Although syntheses of the perfluoro-^[1] perchloro-^[2] and perbromo-^[3] derivatives of naphthalene have been previously described, the periodo-derivative is unknown. We are pleased to report the first synthesis of periodonaphthalene (PIN) using a variation of the permercuration reaction devised by Deacon and Farquharson.^[4] Given its high molecular weight and monoisotopic iodine substituents, PIN is ideal for use as a MS calibration compound. Furthermore, PIN may serve as a pyrolytic precursor to [60]- and [70]-fullerenes.^[5,6]

EXPERIMENTAL

Materials

All chemicals were purchased from Sigma-Aldrich Chemical Company (USA) and used as received.

Physical Measurements

Microanalyses for carbon and hydrogen were performed by Galbraith Laboratories, Knoxville, TN. The mass spectrum was recorded using a Finnigan MAT TSQ700 instrument; the source temperature was approximately 150 °C and the direct exposure probe temperature was ramped to ~ 1000 °C over two minutes; positive ions were detected using chemical ionization (CH₄/3 Torr). The uncorrected melting point was determined in an open capillary using a capillary melting point apparatus.

Synthesis of Periodonaphthalene

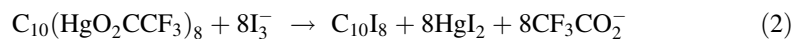
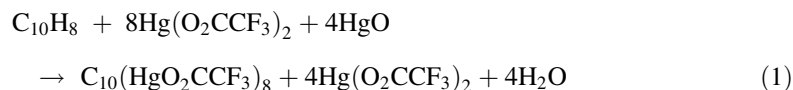
In a typical experiment, mercury(II) trifluoroacetate (50.0 g, 117 mmol) and mercury(II) oxide (3.17 g, 14.6 mmol) were heated to 180 °C and naphthalene (0.469 g, 3.60 mmol) was added through a water-cooled Hempel condenser to the vigorously stirred melt; the naphthalene reacted immediately and sublimation was negligible. Heating was continued for less than one minute. After cooling, the solidified melt was washed into a solution of potassium triiodide [KI (12.3 g, 74.1 mmol) and I₂ (18.8 g, 74.1 mmol) in 150 mL DMF] with 6 × 25 mL DMF and stirred at room temperature in the dark for 7 d. The precipitate, which formed slowly over the course of the reaction, was vacuum-filtered, washed with 3 × 50 mL aq. KBr solution (10% by weight), 3 × 50 mL methanol, and dried in a vacuum



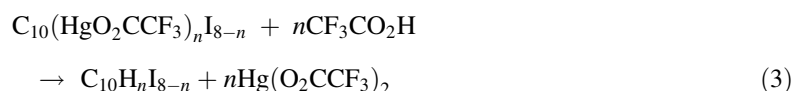
desiccator overnight; 1.23 g of crude product, a mixture of polyiodonaphthalenes, was recovered. After drying, the yellow solid was washed repeatedly with 1-bromonaphthalene until it turned bright orange. The solvent was removed with three acetone washes followed by vacuum drying; 0.522 g of PIN was recovered (12.6% yield) and proved to be insoluble in all common organic solvents. Orange solid, mp ~ 250 °C, dec. with loss of I₂. MS, CI⁺: *m/z* = 1135 (M⁺), 100%; 1009 (C₁₀HI₇⁺), 67.5%; and 883 (C₁₀H₂I₆⁺), 4%. Anal. Calc. for C₁₀I₈ (1135.3): C, 10.58; H, 0. Found: C, 10.89 ± 0.08; H, < 0.5% [For comparison: Anal. Calc. for C₁₀HI₇ (1009.4): C, 11.90; H, 0.10].

RESULTS AND DISCUSSION

PIN was prepared by permercuration of naphthalene in molten mercury(II) trifluoroacetate (Eq. 1), followed by iododemercuration in a triiodide-DMF solution (Eq. 2).



Mercury(II) oxide was added in the reaction of Eq. 1 to consume the liberated trifluoroacetic acid, thereby minimizing protodemercuration,^[7] shown in Eq. 3.



The reaction of trifluoroacetic acid with mercuric oxide is somewhat slower than the reaction of trifluoroacetic acid with polymercurated naphthalene, however, and the low yield of PIN indicates that appreciable protodemercuration, which leads to less substituted iodonaphthalenes, may be occurring in the reaction. In addition, naphthalene is susceptible to dimerization at the melt temperature and its second-order destruction, shown in Eq. 4, may also contribute to a decrease in the yield of PIN.



It is important to note, however, that a low percent yield is acceptable for this reaction; the molecular weight of PIN is approximately nine times



greater than that of naphthalene, the limiting reactant, and the stoichiometry is one-to-one. Thus, with a 10–13% yield, one can expect the mass of PIN recovered to be roughly the same as the mass of naphthalene used in the reaction.

Mass Spectrum

The small homolytic dissociation energy for a C–I bond makes it especially labile when subjected to elevated temperatures and even gentle ionization conditions. Accordingly, the peaks at $m/z = 1009$ and 883 (see Figure 1) are attributable to thermolysis of PIN on the MS sample probe and, to a lesser extent, fragmentation in the ion source; both of these phenomena are well-documented in the mass spectral analysis of perchloronaphthalene.^[8] We were unable, however, to rule out the possibility that these signals are parent peaks of the incomplete iodination products, $C_{10}HI_7$ and $C_{10}H_2I_6$, respectively. A strong molecular ion peak, corresponding to $C_{10}I_8^+$, was observed at $m/z = 1135$.

Elemental Analysis

Quality controls for iodine recovery in the elemental analysis (>95%) allow for significant error in iodine determination for compounds with a large iodine weight percentage. In contrast, the percent weight of carbon

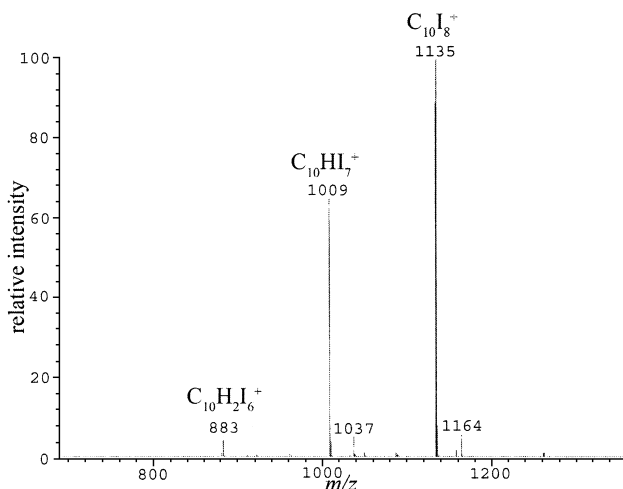


Figure 1. Mass spectrum of PIN.

can be determined accurately and therefore, was used to distinguish between PIN and less substituted polyiodonaphthalenes. The value obtained from the carbon analysis of PIN, 10.89%, matched reasonably well with the calculated value for C₁₀I₈, 10.58%, and any hydrogen present in the sample was below the limit of detection for the method, 0.5% by weight.

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