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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Facile Synthesis of 2,3-Diiodonaphthalene and 2-Bromo-3-iodonaphthalene

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To cite this article: Jonas Hellberg, Fredrik Allared & Margit Pelcman (2003) Facile Synthesis of 2,3-Diiodonaphthalene and 2-Bromo-3-iodonaphthalene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:15, 2751-2756, DOI: <u>10.1081/SCC-120021997</u>

To link to this article: <u>http://dx.doi.org/10.1081/SCC-120021997</u>

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SYNTHETIC COMMUNICATIONS[®] Vol. 33, No. 15, pp. 2751–2756, 2003

Facile Synthesis of 2,3-Diiodonaphthalene and 2-Bromo-3-iodonaphthalene

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ABSTRACT

2,3-Diiodonaphthalene (5) and 2-bromo-3-iodonaphthalene (6) were readily synthesized in two steps by iodination of the corresponding bis(hexachlorocyclopentadiene) adducts 1 and 3 of naphthalene and 2-bromonaphthalene, in methanesulfonic acid, followed by retro Diels-Alder reaction combined with sublimation.

Key Words: 2,3-Diiodonaphthalene; 2-Bromo-3-iodonaphthalene; Iodination; Retro Diels-Alder.

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DOI: 10.1081/SCC-120021997 Copyright © 2003 by Marcel Dekker, Inc. 0039-7911 (Print); 1532-2432 (Online) www.dekker.com

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2,3-Diiodonaphthalene (5) and 2-bromo-3-iodonaphthalene (6) have despite their simplicity rarely been reported in the literature. 2,3-Diiodonaphthalene (5) has been mentioned once without reference to its synthesis^[1] and once in a synthesis from 2,3-diaminonaphthalene yielding 0.5% of 5.^[2] It has also been made by cyclization of 2,3-bis-(iodoethynyl)benzene.^[3] 2-Bromo-3-iodonaphthalene (6) has been synthesized once before, in a multistep synthesis.^[4] Since we needed considerable amounts of **5** in a project directed to annulated dioxins,^[5] and since there should be a interest in these compounds as starting materials for organometallic ligands and as extended π -systems, we decided to develop a new practical synthesis. Our synthesis takes advantage of the propensity of naphthalene bis(hexachlorocyclopentadiene) adduct 1 to undergo electrophilic aromatic substitution in its β -position rather than the more reactive α -position in unsubstituted naphthalene. This has previously been used for the synthesis of several 2-substituted and 2,3-disubstituted naphthalenes.^[6,7] Whereas the brominated derivative 3 is commercially available, iodination of 1 has not been described.

There are numerous methods for iodination of aromatic substrates,^[8] and among the more useful is the Suzuki procedure.^[9,10] Although versatile, this method requires strenous conditions, such as concentrated sulfuric acid as solvent when applied to unactivated aromatics.^[11,12]

Our starting material 1 resisted iodination under both normal Suzuki conditions and in sulfuric acid. We did however observe that 1 has limited solubility in sulfuric acid, which may account for its low reactivity. When performed in methanesulfonic acid, the iodination proceeded smoothly to give high yield of the diiodo derivative 2 when stirring at room temperature overnight or until discoloration (Sch. 1).

The retro Diels-Alder reaction was conveniently performed in a gradient sublimation tube, where **2** was heated to 210° C under vacuum $(1.0-1.5 \times 10^{-2} \text{ mbar})$. Analytically pure 2,3-diiodonaphthalene (**5**) was deposited in a well defined zone in the middle of the tube. Depending on the scale and type of sublimation tube, yields between 50–83% were obtained. The same reaction sequence, starting with the commercially available 2-bromonaphthalene-*bis*(hexachlorocyclopentadiene) adduct (**3**) produced the 2-bromo, 3-iodo intermediate **4** in 98% yield, and the corresponding 2-bromo, 3-iodonaphthalene (**6**) in 40–83% yield respectively (Sch. 2).

In conclusion we have developed a practical and convenient method for the preparation of 2,3-diiodonaphthalene (5) and 2-bromo-3-iodonaphthalene (6).

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Scheme 1.



Scheme 2.

EXPERIMENTAL

The naphthalene-hexachlorocyclopentadiene adducts were purchased from Aldrich. All materials and solvents were used as received. Nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer. Mass spectra were recorded on a **M**1

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Finnigan SSQ. Elemental analyses were performed by Analytische Laboratorien GMBH, Lindlar, Germany.

2,3-Diiodo-*bis*(hexachlorocyclopentadiene)naphthalene Adduct, 2

H₅IO₆, (653 mg, 2.86 mmol) was dissolved in 100 mL methanesulfonic acid at room temperature. After 30 min, I₂ (2.18 g, 8.58 mmol) was added. The flask was equipped with a drying tube and the mixture was allowed to stir for 2 h during which a powerful coloration developed. *Bis*(hexachlorocyclopentadiene)naphthalene adduct 1 (6.73 g, 9.99 mmol) was then added in portions over 5 min, after which the reaction mixture was allowed to stir at room temperature for two days (until discoloration). The pale yellow solution was then poured onto 400 mL ice/water, from which the crude product was collected via filtration after 30 min as a white solid. The material was washed with water and dried, affording **2** (8.43 g, 9.59 mmol, 96%). M.p. 214–217°C (dec.). ¹H-NMR (CDCl₃): δ 8.17 (s, 2H), 3.84 (d, 2H, J = 8.8 Hz), 3.50 (d, 2H, J = 8.8 Hz). ¹³C-NMR (CDCl₃): δ 140.03, 133.51, 130.32, 129.63, 107.26, 101.49, 84.78, 82.50, 46.72, 41.88. MS shows predominatly the M+ peak for the retro Diels-Alder product 2,3-diiodonaphthalene **5**, see below.

2,3-Diiodonaphthalene, 5

The iodinated product 2 (8.21 g, 8.87 mmol) was placed in a gradient sublimation tube. The sublimator was placed so that the vacuum end (outlet to pump) was pointing downward from the hot end-zone. The substance was heated to 210° C, and a vacuum $1.0-1.5 \times 10^{-2}$ mbar was applied. Hexachlorocyclopentadiene soon started to emerge at the vacuum side, and the pure 2,3-diiodonaphthalene (5) deposited slowly higher in the sublimation tube. The starting material also sublimed, forming a band of white crystals well separated from the product. After 1 h, the sublimation was interrupted, and the formed hexachlorocyclopentadiene was poured off, the sublimed starting material was returned to the end of the tube. The sublimation was resumed, and after 1 h the procedure was repeated once more. After completion of the sublimation/retro Diels-Alder reaction, 5 (2.80 g, 7.36 mmol, 83%) was collected as offwhite crystals, and some 2 (486 mg, 0.525 mmol, 6%) as white crystals. M.p. 114.0–114.8°C. ¹H-NMR (CDCl₃): δ 8.40 (s, 2H), 7.67 (m, 2H), 7.48 (m, 2H). ¹³C-NMR: § 138.74, 134.16, 127.57, 127.07, 104.56. MS: 380

SMA.

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(M+78%), 253 (M-I, 24%), 126 (M-2I, 100%). Anal. calcd. for $C_{10}H_6I_2$: C 31.61, H 1.59. Found: C 31.82, H 1.54.

2-Bromo-3-iodo-*bis*(hexachlorocyclopentadiene)napthalene Adduct, 4

H₅IO₆, (655 mg, 2.87 mmol) was added to 100 mL methanesulfonic acid at room temperature. After 30 min, I₂ (2.18 g, 8.58 mmol) was added. The flask was equipped with a drying tube and the mixture was allowed to stir for 2h during which a powerful coloration Bis(hexachlorocyclopentadiene)naphthalene adduct (3, developed. 15.05 g, 20.00 mmol) was then added in portions over 3 min, after which the reaction mixture was allowed to stir at room temperature for four days. The colorless solution was then poured onto ice/water, from which the crude product was collected via filtration after 30 min, as a white solid. The material was washed with water, dried under vacuum, affording 4 as a fine white powder (17.27 g, 19.66 mmol, 98% yield). M.p. 199–200°C (dec.). ¹H-NMR (CDCl₃): δ 8.20 (s, 1H), 7.96 (s, 1H), 3.86 (d, 2H, J = 8.9 Hz), 3.49 (d, 2H, J = 8.9 Hz). ¹³C-NMR (CDCl₃): δ 141.1, 133.5, 133.4, 133.2, 130.7, 129.7, 129.7, 129.6, 129.5, 122.3, 101.5, 100.5, 84.83, 84.82, 82.51, 82.48, 41.90, 41.88, 47.0, 46.6. MS shows predominatly the M+ peak for the retro Diels-Alder product 2-bromo-3-iodonaphthalene (6).

2-Bromo-3-iodonaphthalene, 6

The procedure described for **5** above, starting from **4** (10.00 g, 11.38 mmol) gave **6** (3.16 g, 9.49 mmol, 83%). One hundred and sixty two milligrams (2%) starting material was recovered. M.p. 120.1–120.7°C. ¹H-NMR (CDCl₃) δ 8.39 (s, 1H, CH), 8.13 (s, 1H, CH), 7.69 (m, 2H, CH), 7.50 (m, 2H, CH). ¹³C-NMR (CDCl₃): δ 139.96, 134.08, 133.65, 131.35, 127.77, 127.41, 127.27, 127.01, 126.49, 98.60. MS: 334, 332 (36%/33% M+), 207, 205 (17% M-I), 126 (100% M-BrI).

ACKNOWLEDGMENTS

Financial support from the Royal Institute of Technology and the Ernst Johnson Foundation is gratefully acknowledged.

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Received in the UK November 12, 2002