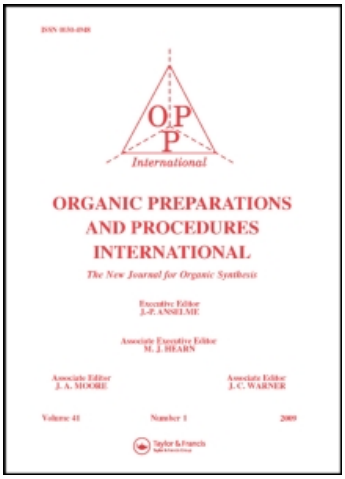

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AN EFFICIENT PREPARATION OF 1,2-DIHYDROCYCLOBUTA[a]NAPHTHALENE

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57-59°, after crystallization from hexane.

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AN EFFICIENT PREPARATION OF 1,2-DIHYDROCYCLOBUTA[a]NAPHTHALENE†

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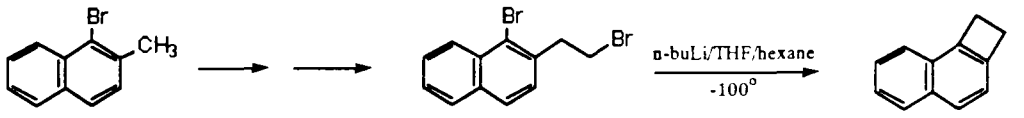
Since the first preparation of 1,2-dihydrocyclobuta[a]naphthalene by Cava and his group via thermal extrusion of sulfur dioxide from 1,3-dihydronaphtho[1,2-c]thiophene-2,2- dioxide,[1] the naphthylcyclobutenes have found increasing potential and use as diene precursors in 1,4-cycloaddition reactions for the construction of polycyclic ring systems and natural products.[2] While there are limited methods available for the preparation of this valuable synthon, our previous use of the Parham cyclialkylation method to prepare a variety of carbocyclic and heterocyclic ring systems[3] indicated that a facile entry to naphthylcyclobutenes should be possible. In view of the continuing use of these compounds in synthesis, herein is described a simple method amenable for the preparation of multigram quantities of 1,2-dihydrocyclobuta [a]naphthalene.



1 2e 3

The requisite starting material for the cyclization, 1-bromo-2-(β-bromoethyl)naphthalene (2e) can be readily prepared from commercially available 1-bromo-2-methylnaphthalene (1) in a straightforward manner as follows. Free-radical bromination of the methylnaphthalene 1 with N-bromosuccinimide and benzoyl peroxide in carbon tetrachloride gives the bromomethyl derivative 2a in 85% yield. Cyanide displacement on 2a gives the naphthylacetonitrile 2b, which is converted to the methylnaphthyl acetate 2c by acid hydrolysis/esterification in a 75% combined

yield. Reduction of 2c with lithium aluminum hydride gives the corresponding alcohol 2d, which upon bromination with 48% hydrobromic acid afforded the desired dibromide 2e in 65% yield (overall yield from 1 = 41%). Selective bromine-lithium exchange of 2e with n-butyllithium occurred readily at -100° in tetrahydrofuran-hexane, and upon warming to room temperature, the naphthylcyclobutene 3 was isolated in 66% yield (27% overall yield from 1).

Based on the current body of literature on the chemistry of functionalized aryllithium reagents,[4] it is clear that this methodology could be extended to prepare a wide variety of naphthylcyclobutenes containing electophilic functional groups which may be difficult to prepare by alternate routes.

EXPERIMENTAL SECTION

1-Bromo-2-(bromomethyl)naphthalene (2a)[5].- To a 1L round bottom flask appropriately equipped were added 1-bromo-2-methylnaphthalene (1; 75.00 g, 0.339 mol), N-bromosuccinimide (81.88 g, 0.460 mol), benzoyl peroxide (0.50 g), and carbon tetrachloride (700 mL), and the mixture was refluxed with stirring for 18 hrs. The mixture was then allowed to cool and the succinimide was filtered and washed with 300 mL carbon tetrachloride. The combined filtrates were concentrated in vacuo to yield 123.38 g of a yellow lachramatory semisolid. Upon treatment of the semisolid with 300 mL hot ethanol, a brown oil separated out of solution, which was decanted away from the ethanol phase. Upon standing, the oil solidified and the resulting solid was recrystallized from methanol to give 22.00 g (wet) of the major by-product, 1-bromo-2-(dibromomethyl)naphthelene as fine white needles, mp. 81-82°; ^{1}H NMR ($CDCl_3$); δ 7.38-8.32 (m, ArH, methine CH).

Anal. Calcd for $C_{11}H_7Br_3$: C, 34.83; H, 1.85; Br, 63.32. Found: C, 35.05; H, 1.77; Br, 63.26

The ethanol triturant, upon cooling, yielded 1-bromo-2-bromomethylnaphthalene (2a; 86.41 g, 85%) as white needles, mp. 103-106°, lit.[5] mp. 103.5-105.5°; ^{1}H NMR ($CDCl_3$): δ 4.86 (s, 2, CH_2), 7.36-8.43 (m, 6, ArH).

1-Bromo-2-(cyanomethyl)naphthalene (2b)[5].- To a 2L round bottom flask appropriately equipped were added a solution of 2a (86.41 g, 0.288 mol) in 1.25L of hot ethanol, potassium cyanide (37.45 g, 0.576 mol), water (300 mL), and the resulting solution was refluxed with stirring for 2 hrs. The mixture wa allowed to cool and was poured into 1.5L of cold water. The resulting precipitate was collected by vacuum filtration to give 1-bromo-2-cyanomethylnaphthalene (2b; 53.82 g, 76%) as yellow needles which were recrystallized from heptane, mp. 124-126.5°, lit.[5] mp. 126.2-127.2°; ^{1}H NMR ($CDCl_3$): δ 4.00 (s, 2, CH_2), 7.41-7.85 (m, 5, ArH), 8.19-8.27 (m, 1, ArH).

1-Bromo-2-(carbomethoxymethyl)naphthalene (2c)[5,6].- To a 500 mL round bottom flask appropriately equipped were added 2b (25.00 g; 0.102 mol), acetic acid (180 mL), 98% sulfuric acid (40 mL) and water (40 mL), and the resulting mixture was refluxed with stirring for 17 hrs.

The mixture was allowed to cool and poured into water (400 mL), and the resulting dark yellow precipitate was isolated by suction filtration (26.92 g, 99%), and the crude product was recrystallized from acetic acid to give fine tan needles (26.56 g, 98%) mp. 194-194.5° (lit.[5] mp. 196-196.2°); ^{1}H NMR ($CDCl_3$): δ 4.05 (s, 2, CH_2), 7.43-7.98 (m, 6, ArH, CO_2H), 8.27-8.37 (m, 1, ArH).

The purified acid (23.70 g, 0.089 mol) was refluxed in a mixture of methanol/98% sulfuric acid (250 mL/20 mL) for 16 hrs. The mixture was allowed to cool to room temperature and was diluted with water (300 mL). The resulting mixture was extracted with methylene chloride (4 x 150 mL) and the organics were dried ($MgSO_4$), and concentrated in vacuo to give the crude product as a brown oil (24.92 g, 100 %), which was virtually pure 2c by ^{1}H NMR analysis; ^{1}H NMR ($CDCl_3$): δ 3.70 (s, 3, CH_3), 4.02 (s, 2, CH_2), 7.30-7.85 (s, 5, ArH), 8.21-8.31 (m, 1, ArH).

1-Bromo-2-(β-hydroxyethyl)naphthalene (2d)[7].- A dry 1L round bottom flask appropriately equipped was charged with lithium aluminum hydride (3.80 g, 0.10 mol) and anhydrous ether (300 mL). The slurry was cooled in an ice bath, and a solution of the crude ester 2c (24.92 g, 0.089 mol) in 300 mL anhydrous ether was added dropwise over a 4 hr period under nitrogen, after which the reaction mixture was refluxed with stirring for 1.5 hrs. The mixture was then cooled in an ice bath and was carefully hydrolyzed by the slow addition of water (15 mL), 15% sodium hydroxide (30 mL), and water (40 mL). The resulting granular mass was filtered and washed with 200 mL ether. Concentration in vacuo of the combined filtrate and washing yielded 19.28 g (86%) of 1-bromo-2-(β-hydroxyethyl)naphthalene (2d) as a yellow oil virtually pure by ^{1}H NMR analysis; ^{1}H NMR ($CDCl_3$): δ 2.65 (bd s, 1, exchangeable OH), 2.97 (t, 2, CH_2CH_2), 4.67 (t, 2, CH_2), 7.00-7.52 (m, 5, ArH), 8.05 (d, 1, ArH).

1-Bromo-2-(β-bromoethyl)naphthalene (2e).- To a 500 mL round bottom flask appropriately equipped were added 2d (19.28 g, 0.0768 mol) and 48% hydrobromic acid (250 mL), and the resulting mixture was refluxed with stirring for 24 hrs. The mixture was permitted to cool and was extracted with methylene chloride (5 x 100 mL). The methylene chloride extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo to give 21.87 g (91%) of a pale brown oil which was distilled in vacuo to yield pure 1-bromo-2-(β-bromoethyl)naphthalene (2e) as a water-white oil (18.22 g, 76%), bp. 152-155°/0.07 torr; IR (film): 3060, 2940, 1600, 1560, 1500, 1260, 1220, 960, 820, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.52 (overlapping triplets, 4, CH_2CH_2), 7.12-7.76 (m, 5, ArH), 8.23 (d, 1, ArH).

Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.86; H, 3.18; Br, 50.96 Found: C, 45.64; H, 3.21; Br, 50.71

Preparation of 1,2-Dihydrocyclobuta[a]naphthalene(3).- A solution of 2e (6.28 g; 0.02 mol) in dry tetrahydrofuran (125 mL) and hexane (25 mL) was placed into a 250 mL three-neck round bottom flask provided with a mechanical stirrer and having a static dry nitrogen atmosphere and was cooled to -100°. n-Butyllithium (9.20 mL, 0.022 mol/2.45M in hexane) was added via a pressure- equalizing adition funnel at such a rate that the temperature did not exceed -95°, and

after the completion of the addition the reaction mixture was stirred at -100° for 1 hr and was permitted to warm to room temperature. The mixture was then poured into water (250 mL) and the organic phase was separated. The aqueous phase was extracted with ether (3 x 100 mL) and the combined organics were dried ($MgSO_4$), filtered, and concentrated in vacuo to give 2.99 g of a brown oil which was distilled in vacuo to give pure 1,2-dihydrocyclobuta[a]naphthalene (2.05 g, 66%) as a water-white oil, bp. 99-100°/1.70 torr (lit.[1] bp. 98°/1-2 torr); ^1H NMR ($CDCl_3$): δ 3.20-3.40 (overlapping t, 4, cyclobutene CH_2), 7.08-7.81 (m, 6, ArH).

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