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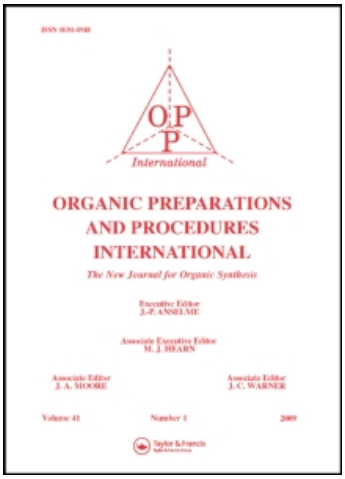

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THE LITHIATION OF 1,4-DIMETHOXYNAPHTHALENE AND CARBOXYLATION OF THE PRODUCTS

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THE LITHIATION OF 1,4-DIMETHOXYNAPHTHALENE AND CARBOXYLATION OF THE PRODUCTS

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In studies designed to prepare 5,8-dimethoxy-1-naphthoic acid (1), the lithiation of 1,4-dimethoxynaphthalene (II) followed by carboxylation was examined. In our best attempt about 50% of methyl 5,8-dimethoxy-1-naphthoate (III), 25% of methyl 1,4-dimethoxy-2-naphthoate (IV), 10% of 1,4-dimethoxynaphthalene-2,5-dicarboxylic acid (V), in addition to 12% of recovered II were isolated from the mixture of compounds produced.

EXPERIMENTAL SECTION

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Lithiation and Carboxylation of 1,4-dimethoxynaphthalene.- An ice-cooled, stirred mixture of 350 mL of 1.7 M t-butyllithium in pentane (0.6 mole) and 300 mL of dry cyclohexane was prepared in a 3-neck flask under nitrogen. To this solution was added over 5 minutes 94.0 g of 1,4-dimethoxynaphthalene in 800 mL of warm cyclohexane (0.5 M). The resulting mixture, which contained a thick yellow-brown salt, was stirred for 72 hrs., and then combined with a stirred mixture of Dry Ice and ether. The alkaline product solution was extracted with ether to recover 11.7 g (12%) of II. The crude acids, obtained on pouring into ice and hydrochloric acid, amounted to 105 g.

Separation of Crude Acid Mixture.- A mixture of 32 g of sodium hydroxide, 3.2 g of tetrabutylammonium bromide, and 800 mL of dichloromethane were stirred and refluxed with 50 g of the powered crude acid for 15 hrs. Then, 38 g of dimethyl sulfate in 30 mL dichloromethane was added over 30 min. The organic layer was separated, washed with 10% sodium hydoxide solution, and dried over magnesium sulfate. On concentration, 47.5 g of mixed esters were obtained. After acidification, the alkaline washings yielded 7.0 g (10%) of V, mp. 222-224°, as a colorless solid after recrystallization from boiling water. NMR (acetone-d_6): δ 8.30 (dd, j_o = 8, j_m = 1.6), 7.66 (dd, 7-H, j_o = 7), 7.62 (dd, 6-H, j_o = 7.0, j_m = 1.6), 7.33 (s, 3-H), 4.02 (s, OCH_3), 3.97 (s, OCH_3). MS: 276.0632.

Anal. Calcd. for $C_{14}H_{12}O_6$: C, 60.9; H, 4.4. Found: C, 60.5; H, 4.7

The crude mixture of esters was extracted with 800 mL of boiling hexane to yield as insoluble a total of 29.8 g (50%) of colorless III, mp. 103-104°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.4; H, 6.0

Vacuum distillation of the product remaining in the neutral fraction from the above esterification yielded IV, bp. 175-176°/1.5 mm, as colorless needles, mp. 54.5-55.5°, lit.[1] mp.

57-59°, after crystallization from hexane.

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† Postdoctoral Research Associate supported by a grant from the NIH, CA 07394.

1. A. H. Homeyer and V. H. Wallingford, J. Am. Chem. Soc., 64, 798 (1942).

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

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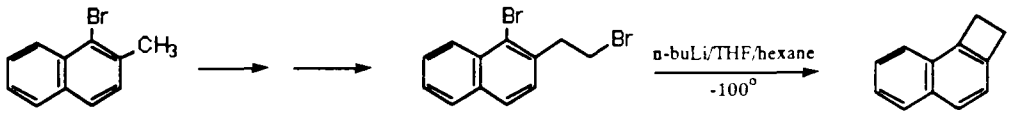
Since the first preparation of 1,2-dihydrocyclobuta[a]naphthalene by Cava and his group via thermal extrusion of sulfur dioxide from 1,3-dihydronaphtho[1,2-c]thiophene-2,2- dioxide,[1] the naphthylcyclobutenes have found increasing potential and use as diene precursors in 1,4-cycloaddition reactions 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