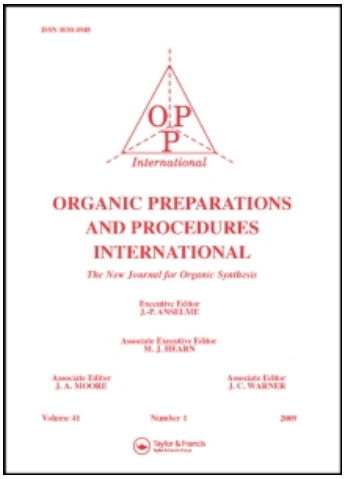

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A FACILE SYNTHESIS OF 6,7-DIHYDRO-5H-DIBENZO[a,c]CYCLOHEPTENE

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A FACILE SYNTHESIS OF 6,7-DIHYDRO-5H-DIBENZO[a,c]CYCLOHEPTENE

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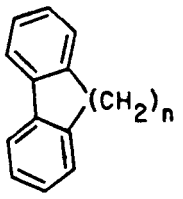
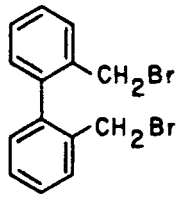
The 2,2'-bridged biphenyls 1a-e are important substrates in a number of physico-chemical studies.[1] The 2,2'-bridged biphenyl 1c has also been used as a reference compound for several photoelectron spectroscopic investigations.[2] While nine syntheses of 6,7-dihydro-5H-dibenzo[a,c]cycloheptene (1c) have been reported,[3-5] they are less than satisfactory. Only the route described by Cope and Smith[3] has provided 1c in greater than 30% overall yield (32% in four steps from the non-commercially available 2). The most convenient and widely used synthesis[4] of 1c provides a 27% overall yield of 1c in seven steps from 2-(2'cyanophenyl)-benzoic acid (3) which in turn can be prepared from the monooxime of phenanthrenequinone.



1a-e n = 1-5



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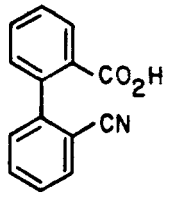
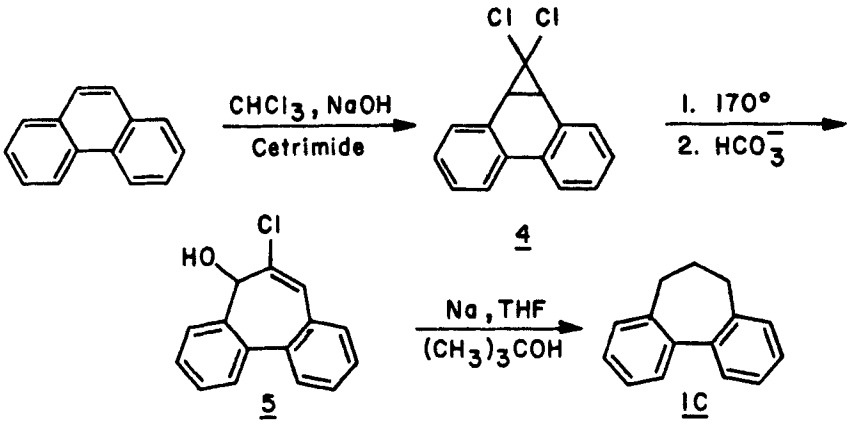


3

We now report a facile, high-yield synthesis of 1c which proceeds in four steps from phenanthrene.

7,7-Dichlorodibenzo[a,c]bicyclo[4.1.0]heptane (4) can be obtained in multi-gram quantities by the phase-transfer addition of dichlorocarbene to phenanthrene (79% based on recovered phenanthrene) according to the procedure of Joshi, Singh and Pande.[6] The use of the cationic detergent cetyltrimethylammonium bromide (0.7 g to 100 g of phenanthrene) is critical

for high yields of 4. Quantitative conversion of the dibenzodichloronorcarane 4 to the chloro alcohol 5 is then readily



accomplished in a one-pot reaction sequence which involves heating a melt of 4 at 170° for 30 min. followed by alkaline hydrolysis in acetonitrile.[7] Treatment of 5 under the Gassman-Pape[8,9] conditions (Na, 2-methyl-2-propanol, THF) results in reduction to the title compound (1c) in 87% yield. This latter reduction takes advantage both of the propensity of the Gassman-Pape conditions to result in reduction[10,11] as well as dechlorination when applied to vinyl chlorides and the facile reductive cleavage of benzylic and allylic alcohols.[12-14] Preparative quantities of 1c can thus be readily obtained in 69% overall yield from commercially available phenanthrene.

EXPERIMENTAL SECTION

6,7-Dihydro-5H-dibenzo[a,c]cycloheptane (1c).- To a solution of 6-chloro-5H-dibenzo[a,c]cyclohepten-5-ol (5, 2.4 g, 9.93 mmol) in 320 ml of dry tetrahydrofuran was added 6.4 g (86.5 mmol) of 2-methyl-2-propanol and 6.1 g (265.2 mmol) of sodium metal. The reaction mixture was heated at reflux for 24 hrs. then cooled to room temperature. The unreacted sodium was removed by filtration and the solution was concentrated in vacuo. The

resulting orange oil was dissolved in 270 ml of ether, combined with 70 ml of water and acidified with 10% HCl. The aqueous layer was then extracted with a second portion of ether (75 ml) and the ethereal extracts were washed with 10% $NaHCO_3$ and brine. The combined ethereal extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo to yield 1.73 g (87%) of 1c as an oil which solidified on standing, mp. 52.7-54.3°, lit.[4] 54.5-55.0°. The isolated material was spectroscopically identical with the previously reported data.[1c,5f]

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ORGANIC SONOCHEMISTRY. A FACILE SYNTHESIS OF 1-METHYLISOQUINOLINE

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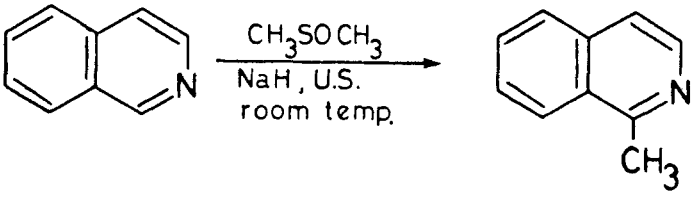
1-Methylisoquinoline has been prepared mainly by catalytic dehydrogenation of 1-methyl-3,4-dihydroisoquinoline obtained by Bischler-Napieralsky reaction,[1] or by alkylation of the isoquinoline Reissert compound.[2] As the latter procedure could not be performed by our group under phase-transfer catalysis,[3] we have adapted an interesting procedure



from Russell and Weiner[4] by generating methyl sulfinyl carbanion ("Corey base") under ultrasound[5] in the presence of isoquinoline. The method (72-