Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Sep 2006.

To cite this article: B. Serge Kirkiacharian & Pantelis G. Koutsourakis (1993): Hydroborations: A New Route for the Preparation of 1-Alkyl- (or Aryl) 2-Tetralones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:6, 737-742

To link to this article: http://dx.doi.org/10.1080/00397919308009833

SYNTHETIC COMMUNICATIONS, 23(6), 737-742 (1993)

HYDROBORATIONS : A NEW ROUTE FOR THE PREPARATION OF 1-ALKYL- (OR ARYL) 2-TETRALONES

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ABSTRACT: The hydroboration followed by chromic acid oxidation of 1-alkyl- and 1-aryl-3,4-dihydronaphthalenes leads to the corresponding 1-alkyl- (or aryl)2-tetralones (1-substituted 3,4-dihydronaphthalen-2(1H)-ones) .

The 1-substituted 2-tetralones (1-substituted 3,4-dihydronaphthalen-2(1H)-ones) **2** , are starting compounds for the preparation of various terpenes, [1,2] analgesic molecules derived from benzomorphan,[3] estrogens[4] and antiandrogens.[5] As a part of a synthetic program of potential biologically active compounds, we required 1-substituted 1-alkyl and 1-aryl-2-tetralones. A survey of the literature, indicated that their preparation usually performed by oxidation of 1-substituted 3,4-dihydronaphthalenes with lead oxide, lead acatate[2] or peracids[5-12], or by C- alkylation procedures at position 1 of 2-tetralones, give generally either medium to low overall yields,[13,14] or mixtures of mono and

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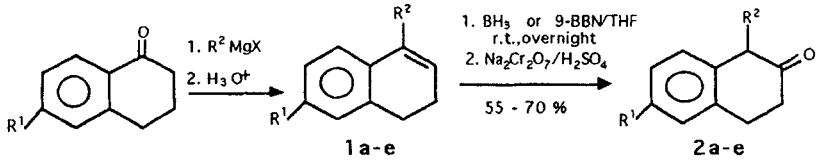
scheme



1 , 2	R^1	R^2
a	H	CH_3
b	H	C_2H_5
c	H	C_6H_5
d	CH_3O	CH_3
e	CH_3O	C_6H_5

dialkylated compounds.[15] The availability of a general route for the preparation of various substituted 1-alkyl and 1-aryl-2-tetralones would thus be of interest . We therefore developed a new route via a Grignard reaction, on 1-tetralone and 6-methoxy-1-tetralone, to the known 1-alkyl-(or aryl)3,4-dihydro-naphthalenes **1a-e**, followed by hydroboration and chromic acid oxidation[16] .

The hydroboration was carried out either with borane-THF complex (derivatives **1a-b**) or with 9-BBN-THF (derivatives **1c-e**). In all cases, the expected 1-substituted 2-tetralones **2a-e** were obtained after the oxidation step (scheme).

The ketones were purified by distillation under reduced pressure or by column chromatography over silica . Their structures were established by

elemental analysis , infrared and ^1H NMR spectroscopy . All derivatives gave the expected 2,4-dinitrophenylhydrazones (DNPH) .

Experimental Section

Melting and boiling points are uncorrected. I R spectra were recorded on a Perkin -Elmer 177 spectrometer and ^1H NMR spectra on a Varian T 60 spectrometer . Glass equipments were dried at 100°C in an oven prior to use . THF-BH_3 and THF-9-BBN are commercially available (Aldrich) . THF was distilled from benzophenone ketyl.

1-Methyl-2-tetralone 2a .Typical Procedure A. To a nitrogen flushed 100 mL round bottom flask , THF . BH3 solution (30 mL , 10 mmol) is added dropwise , with a syringe via a septum inlet , to a cooled solution (0-5°C) of 1-methyl-3,4-dihydronaphtalene (2.88 g , 20 mmol) dissolved in dry THF (100 mL) . The reaction is left to come to r.t. , while stirring is continued overnight . The excess of hydride is then destroyed by careful addition of water drops , the THF is evaporated and Et_2O (100 mL) is added . A chromic acid solution, prepared from $Na_2Cr_2O_7$, $2H_2O$ (4.43 g , 15 mmol) and 96% sulfuric acid (3.4 mL , 59 mmol) diluted with water to 19 mL , is added to the stirred etheral solution over a period of 15 min . After refluxing for 2 hours , the Et_2O layer is separated and the aqueous layer extracted with Et_2O (3x 50 mL) . The combined organic extracts are then washed with brine to neutral and dried (Na_2SO_4) . After filtration , the solvent is removed and the residue distilled under reduced pressure .

Yield 2.20 g b.p. 106°C/0.08;($C_{11}H_{12}O$) ; Yield 73%; oil, ; . ^{1}H NMR ($CDCl_3$ / TMS) : 1.2, (d, 3H, J = 6Hz, CH3) ; 1.9, (d, 1H, J = 6Hz, CH) ;2.5-3.0, (m, 4H, 3,4 -CH_2 - CH_2) ; 6.8- 7.3, (m, 4H, arom.) ; I.R. : 3420, 1720; DNPH: 148°C (ethanol).

1-Ethyl-2-tetralone 2b .Prepared with the procedure A.The Product is separated by column chromatography over silica (solvent DCM-EtOH : 98-2) ; ($C_{12}H_{14}O$); Yield: 55 %; oil ; ^{1}H NMR ($CDCl_3$ / TMS): 1.0, (t, 3H, J = 7Hz, CH_2 - CH_3) ;1.2 - 3.0, (m, 7H, CH, 3,4 - CH_2 - CH_2, CH_2 - CH_3) ;7.2, (m, 4H, arom.) ; I.R.: 3430, 1680; DNPH : 153°C (ethanol)

1-Phenyl-2-tetralone 2c .Typical procedure B . The reaction is performed as given under procedure A with 1-phenyl-3,4-dihydronaphtalene (2.06 g , 10 mmol) and a 0.5 molar THF- 9-BBN solution (22 mL , 11 mmol) . The oxidation is carried out with a solution of $Na_2Cr_2O_7$, $2H_2O$ (6.9 g , 23 mmol) , 96% sulfuric acid (5.2 mL , 93 mmol) , diluted to 30 mL with water during 2 hours .The mixture is worked up as for procedure A . Product **2c** is separated by column chromatography over silica (solvent DCM-EtOH : 98-2) ($C_{16}H_{14}O$); Yield: 53%; oil ; 1H NMR ($CDCl_3$ / TMS): 2.3, (s, 1H, CH) ; 2.6, (dd, 2H, J1 =2Hz, J2 = 3Hz, 3 - CH_2) ; 2.8, (dd, 2H, J1 =2Hz, J2 = 3Hz, 4 - CH_2) ; 7.8, (m, 9H, arom.); DNPH: I.R.: 3680, 1680; 156°C(ethanol).

The preparation of compounds **2d** and **2e** is performed with the procedure B.

1-Methyl-6-methoxy-2-tetralone 2d.(C12 H14 O2); Yield : 69 %; oil: b.p.:112 / 0,07; 1H NMR (DMSO D6 / TMS): 1.3, (d, 3H, J = 5Hz, CH3) ;

2.9, (dd, 2H, J =2Hz, J2 = 3Hz, 3 - CH2) ; 3.2, (dd, 2H, J1 = 2Hz, J2 = 6Hz, 4 - CH2) ; 3.8, (s, 3H, OCH3) ; 6.5 - 8.0, (m, 3H, arom.) ; 9.8, (s, 1H, OH: enol exchangeable)) ; I.R.: 3680, 1680 DNPH 151°C (ethanol)

1-Phenyl-6-methoxy 2-tetralone 2e. (C_{17} H_{16} O_2); Yield : 59 %; ^{1}H NMR (DMSO D6 / TMS): 2.8, (m, 4H, 3,4 - CH_2 - CH_2) ; 3.8, (s, 3H, OCH3) ; 6.5 - 7.8, (m, 8H, arom.) ; 9.0, (s, 1H, OH: enol exchangeable)) ; I.R. : 3680,1690; DNPH: 172°C (ethanol).

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(Accepted in The Netherlands 29 September, 1992)