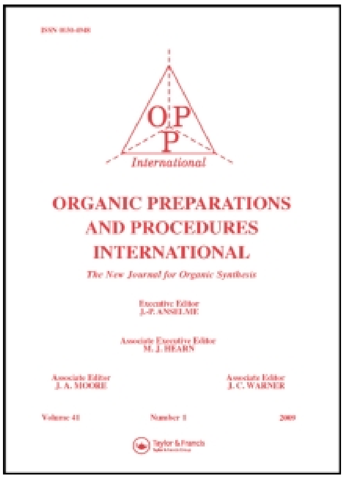
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

1,2,3,4-TETRAHYDRO-1,4,d_2-NAPHTHALENE-1,4.5,6,7.8.-d_6

Mark H. Gaston[a]; Duane R. Skidmore[b]
[a] Analytical Sciences Branch, Morgantown Energy Technology Center, Oak Ridge Associated Universities, Morgantown, WV [b] Department of Chemical Engineering, The Ohio State Univeristy, Columbus, OH

To cite this Article Gaston, Mark H. and Skidmore, Duane R.(1985) '1,2,3,4-TETRAHYDRO-1,4,d_2-NAPHTHALENE-1,4.5,6,7.8.-d_6', Organic Preparations and Procedures International, 17: 2, 138 — 140
To link to this Article: DOI: 10.1080/00304948509355486
URL: http://dx.doi.org/10.1080/00304948509355486

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

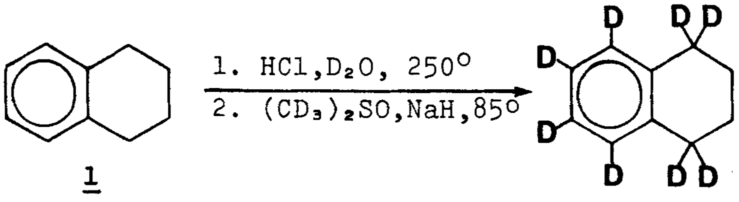
1,2,3,4-TETRAHYDRO-1,4,d_2-NAPHTHALENE-1,4,5,6,7,8,-d_6

Submitted by Mark H. Gaston[†] and Duane R. Skidmore[††]*
(04/06/84)

[†]Oak Ridge Associated Universities
Analytical Sciences Branch
Morgantown Energy Technology Center
P.O. Box 880, Morgantown, WV 26505

[††]Department of Chemical Engineering
The Ohio State Univeristy, Columbus, OH 43210

Proposed research on coal liquefaction necessitated the preparation of deuterium-labelled tetralin in gram quantities. Previously the most common technique for preparing highly deuterated tetralin involved exchange of naphthalene with a labelled strong acid, e.g., D_3PO_4, followed by catalytic hydrogenation with D_2.[1] In this work, high-pressure hydrogenation with D_2 was avoided by using tetrahydronaphthalene (1) as a starting material. Werstiuk has prepared several deuterated aromatic hydrocarbons under conditions of dilute acid and high temperature.[2] This method was used to effect exchange in the 5,6,7 and 8 positions of 1. The mild conditions employed left the aliphatic ring intact. Chen *et al.*[3] have synthesized several CD_3 substituted benzenes by exchanging the analogous methylbenzenes with $(CD_3)_2SO$ over NaH. This procedure was adapted to exchange 1,2,3,4-tetrahydronaphthalene-5,6,7,8-d_4 in the first and fourth positions.



From the ^{2}H-NMR spectra it was concluded that exchange occurred exclusively in the aromatic and at the first and fourth positions. The average molecular formula was estimated ^{1}H-NMR and MS to be $C_{10}H_{6.39}D_{5.61}$. The extent of incorporation was estimated at 61.1 percent in the aromatic and

79.3 percent in the first and fourth positions. Although this was sufficient for our subsequent work,, a much higher isotopic purity can be achieved by repeating the exchange reaction.

EXPERIMENTAL SECTION

GC-MS spectra were obtained using a Finnigan 4021 instrument. Electron impact ionization was used for structural confirmation and chemical ionization with CH_4 was used to determine relative abundances of the molecular ions. FT-NMR spectra (7 tesla) were obtained using a Bruker WM-300 spectrometer. Tetrahydronaphthalene was purchased from Alpha Products and distilled at reduced pressure before use. All reaction were carried out under a nitrogen atmosphere.

Deuteration of Naphthalene.- A mixture of 4 g (30.3 mmol) of tetrahydronaphthalene (1), 4 ml of D_2O and four drops of conc. hydrochloric acid was degassed by three freeze-thaw cycles and sealed in a glass tube. The tube was heated in an autoclave to 250° for 48 hrs. To equalize the internal pressure the autoclave was pressurized to 650 psi with nitrogen. After completion of the reaction, the product was drawn off with a pipet and dried over $MgSO_4$ and then Na. This process was repeated to yield 6.5 g of 1,2,3,4-tetrahydronaphthalene-5,6,7,8-d_4 [MS (70 eV): m/e 132-136 (M^+)]. This product was combined with 7.7 g (91.6 mmol) of DMSO-d_6 and vacuum transferred onto 0.6 g of NaH, prepared by washing a dispersion of NaH in mineral oil with heptane. The mixture was stirred for 30 hrs at 85°, after which the exchanged liquids were vacuum transferred to a Dry Ice cooled trap. Removal of the DMSO by extraction with 80 ml of water gave 4.85 g (73%) of 2.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28 (1.55H), 2.97 (0.83H), 2.01 (4H); ^{2}H-NMR (45 MHz, $CHCl_3$): δ 7.25, 2.94; MS (70 eV): m/e 132-140 (M^+).

Acknowledgement.- We thank Mary Ann Siefert and Dr. Charles Cottrell who ran the GC-MS and NMR spectra. Helpful discussions with Dr. C. Richard Weisenberger regarding the mass spectra are gratefully acknowledged. Use of the NMR spectrometer was funded in part by National Science Foundation Grant CHE910019.

REFERENCES

1. R. P. Skowronski, J. J. Ratto, and L. A. Heredy, Annual Technical Progress Report to DOE, FE-2328-13, 1978, pp. 52-56.
2. N. H. Werstiuk and G. Timmins, Can. J. Chem., 59, 3218 (1981).
3. T. S. Chen, J. Wolinska-Mocydlarz, and L. C. Leitch, J. Labelled Compounds, 6, 285 (1971).
4. The total vapor pressure at 250° was taken as the sum of that for water (576.6 psia) and tetrahydronaphthalene (36.2 psia). The latter value was taken from M. Kara, S. Sung, E. Klinzing, and S. K. Chiang, Fuel, 60, 633 (1981).

ONE-POT SYNTHESIS OF NITROSTYRENE OXIDES

Submitted by Karim Rafizadeh and Keith Yates*
(07/23/84)
Department of Chemistry, University of Toronto
Toronto, Ontario, CANADA M5S 1A1

There has been considerable interest in recent years in nitrostyrene oxides and in products derived from them. For instance, *o*-nitrostyrene oxide has been used as a precursor in the synthesis of *o*-nitrophenylethylene acetal or ketal, a photoremoveable protective group for aldehydes and ketones.[1,2] It has also been used in the synthesis of benzisoxazolone, an antibacterial and antileukemic agent.[2] A mechanistic study of the ring opening of nitrostyrene oxides was the subject of another series of articles.[3] Nitrostyrene oxides have usually been made *via* lengthy, laborious or costly methods. There are essentially two existing methods for their synthesis in the literature. The first involves the reaction of diazomethane with nitrobenzaldehydes[4] while the second includes