Convenient Synthesis of Perinaphthane via Chloroaluminum Hydride Reduction of Perinaphthanone[1]

J. Ernest Simpson

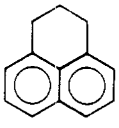
Department of Chemistry, California State Polytechnic University, Pomona, California 91768

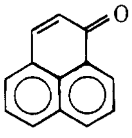
Guido H. Daub*

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

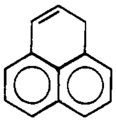
Received September 12, 1978

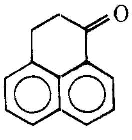
As part of a project involving the synthesis of ^{13}C labeled benzo[*a*]pyrenes we had need for pure perinaphthane (**1**) which has been prepared from perinaphthenone (**2**), perinaphthene (**3**), and perinaphthanone (**4**). Reduction of perinaphthenone (**2**) affords perinaphthane (**1**) via high-pressure hydrogenation over copper chromite in yields of 70–80%;[2,3] however, the success of these reductions is largely dependent on the ketone/catalyst ratio and the purity of **2** used. Hydrogenation of perinaphthene (**3**) is reported to give **1** in excellent yield;[4,5] however, the preparation of **3** from **2** proceeds in poor yield[4] and its synthesis from perinaphthanone (**4**) in two steps as well as other miscellaneous methods were unsuitable for our needs.[5] Perinaphthanone (**4**), which is available from 1-(chloromethyl)naphthalene,[6] has been converted to **1** via the Clemmensen method[3,6] in 12% yield or in 46% yield by hydrogenation over Pd/C in acetic acid at 2 atm.[7] Attempts to prepare perinaphthanone (**4**) from perinaphthenone (**2**) by the method of Dokunikhin[8] failed, the net result being that reported earlier by Fieser and Hershberg.[2] Reduction of **2** using 5% Pd/C in ethyl acetate at room temperature afforded mainly perinaphthanol (**5**).


1

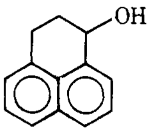


2


3



4



5

We wish to report a highly successful synthesis of **1** from **4** via reduction with lithium aluminum hydride and aluminum chloride in ether.[9] Using a molar ratio of LiAlH$_4$/AlCl$_3$ of 0.5 in the reduction affords 91–97% yields of perinaphthane (**1**) of good quality in runs using from 1 to 20 g of **4**. The quality of the **4** used does not appear to be critical with respect to the yields of **1** obtained. The crude perinaphthane (**1**) was readily purified by column chromatography over silica gel to give material of equal of better quality than that obtained by high-pressure hydrogenation of perinaphthenone followed by fractional distillation.[2,3] We feel that the preparation of perinaphthane by the reduction of perinaphthanone with LiAlH$_4$/AlCl$_3$ in ether as described here is superior to other methods used for the preparation of **1**.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^{1}H-NMR spectrum of **1** was measured on a Hitachi Perkin-Elmer Model R-24 spectrometer using Me$_4$Si as an internal standard, and the ^{13}C NMR was recorded on a Varian Model CFT-20 spectrometer. Reactions were monitored and product purity was checked by thin-layer chromatography on precoated silica gel plates (EM Laboratories 60F-254) using benzene as a developing solvent. The compounds and their approximate R_f values were as follows: **1** (0.64), **2** (0.05), **4** (0.15), **5** (0.19).

Perinaphthane (1). A 300-mL three-necked flask equipped with a condenser, addition funnel, and magnetic stirrer was flushed with dry N$_2$ and charged withLiAlH$_4$ (3.22 g, 84.8 mmol) and 50 mL of anhydrous ether. To this mixture was added over a 10–15-min period a solution of AlCl$_3$ (22.8 g, 171 mmol) in 80 mL of anhydrous ether (prepared by adding ether dropwise with stirring to the AlCl$_3$ in an Erlenmeyer flask equipped with a dropping funnel, reflux condenser, and drying tube). To this mixture a solution of 9.0 g (49.4 mmol) of perinaphthanone (**4**),[6] mp 76–80.5 °C, in 70 mL of anhydrous ether was added over a period of 45 min while sustaining a gentle reflux. The reaction mixture was refluxed for an additional 2 h, after which time 5 mL of ethyl acetate was added slowly to the cooled reaction mixture to destroy the excess LiAlH$_4$. The reaction mixture was poured over ice (600 mL), and the ether layer was washed with water and dried over anhydrous MgSO$_4$. Removal of the ether afforded a pale yellow solid, mp 60.5–65 °C, in quantitative yield. The crude product was taken up in cyclohexane and chromatographed over silica gel (EM Laboratories 230–400 mesh) in a 25 × 190 mm column. Elution with cyclohexane gave a slightly fluorescent colorless band which was collected in 125 mL of eluent. Removal of the cyclohexane afforded colorless **1** (7.61 g, 92%), mp 62.5–65 °C. One recrystallization from 60 mL of methanol yielded perinaphthane (**1**) as colorless plates (82% recovery), mp 66–67 °C (lit.[2] mp 65.4 °C). An additional colorless crop (10%, mp 64–65.5 °C) was obtained from the mother liquor. Since **1** is light sensitive, the chromatography and other purification steps were carried out in subdued light. The ^{1}H-NMR spectrum of **1** was identical to that reported by Shannon and Cox,[10] and the ^{13}C-NMR spectrum (CCl$_4$) matched that reported by Hunter and Stothers.[11]

Acknowledgments. This investigation was supported in part by Grant No. CA-16871 awarded by the National Cancer Institute, DHEW. We also thank Dr. Thomas W. Whaley of Group H-11 and the Los Alamos Scientific Laboratory for the NMR spectra.

Registry No.—**1**, 479-58-3; **2**, 548-39-0; **3**, 203-80-5; **4**, 518-85-4.

References and Notes

(1) Supported in part by Grant No. CA-16871 from the National Cancer Institute, DHEW.
(2) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 1658 (1938).
(3) I. K. Lewis and R. D. Topsom, *Aust. J. Chem.*, **18**, 923 (1965).
(4) G. Lock and G. Gergely, *Ber.*, **77B**, 461 (1944).
(5) V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1245 (1950).
(6) L. F. Fieser and M. D. Gates, *J. Am. Chem. Soc.*, **62**, 2335 (1940).
(7) C. Heidelberger and H. S. Rieke, *Cancer Res.*, **11**, 640 (1951).
(8) N. S. Dokunikhin, S. L. Solodar', and A. V. Reznichenko, *Zh. Org. Khim.*, **12**, 379 (1976).
(9) For references to mixed hydride reductions see: (a) E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, **88**, 729 (1966), and references therein; (b) J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1405 (1961); (c) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964), and references therein; (d) R. M. Pagni and C. R. Watson, *Tetrahedron*, **29**, 3807 (1973).
(10) R. L. Shannon and R. H. Cox, *Tetrahedron Lett.*, 1603 (1973).
(11) D. H. Hunter and J. B. Stothers, *Can. J. Chem.*, **51**, 2884 (1973).

Thermal Decomposition of Aluminum Alkoxides

Gottfried Brieger,* Stephen W. Watson, Donald G. Barar, and Anita L. Shene

Department of Chemistry, Oakland University, Rochester, Michigan 48063

Received March 3, 1978

Numerous methods are available for the dehydration of alcohols, including the conventional approaches using acid catalysts, as well as a variety of more specialized thermal methods including the Hofmann elimination, amine oxide, xanthate, and acetate pyrolysis.[1] None are universally applicable and in fact often give poor yields or unmanageable