

PERDEUTERATION AT THE 9,10-POSITIONS OF 9,10-DIBROMOANTHRACENE AND ANTHRACENE- d_{10}

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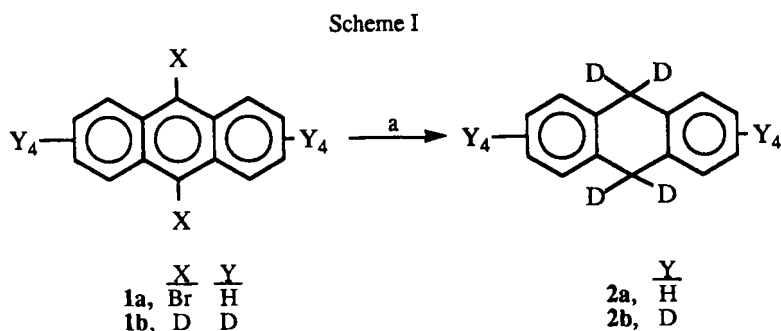
SUMMARY

Na/D₂O/THF is highly effective in perdeuteration of anthracene- d_{10} and 9,10-dibromoanthracene at the 9,10-positions to give 9,10-dihydro-9,10- d_2 -anthracene- d_{10} and 9,10-dihydro-9,9,10,10- d_4 -anthracene respectively.

Key Words: 9,10-Dihydro-9,10- d_2 -anthracene- d_{10} , 9,10-dihydro-9,9,10,10- d_4 -anthracene, sodium, deuterium oxide, reduction.

INTRODUCTION

As part of an effort at the National Institute for Petroleum and Energy Research to obtain statistical thermodynamic properties of organic molecules from fundamental vibrational frequencies, assigned through spectroscopic studies, gram quantities of deuterium-labeled compounds with a high percentage of deuterium incorporation were needed. The first of these, 9,10-dihydro-9,9,10,10- d_4 -anthracene [2a] and 9,10-dihydro-9,10- d_2 -anthracene- d_{10} [2b] were prepared by reduction of 9,10-dibromoanthracene [1a] and anthracene- d_{10} [1b], respectively, as shown in Scheme I.



^aNa, THF, D₂O, Δ.

The usual methods for deuterium incorporation at these positions involve metal-, acid-, or base-catalyzed exchange between an unlabeled hydrocarbon and deuterium oxide (1). Considering the quantities needed and to avoid the repetitive and more costly exchange processes, a single-stage, high-yield deuteration process was sought.

Reduction of 9,10-dibromoanthracene [**1a**] with Na/C₂H₅OD gave **2a** contaminated with starting material. A second reduction was required to completely eliminate **1a**. Survival of unreacted starting material has been reported for similar reductions of anthracene and **1b**. Reduction with H₂O or D₂O in ether was incomplete. Substitution of THF for diethyl ether improved the solubility of the starting materials and the resulting reaction (Na - D₂O/THF) completely reduced **1a** to **2a**. The reduction did not proceed beyond the 9,9,10,10-tetradeutero stage nor was anthracene reduced beyond 9,10-dihydro-9,10-d₂-anthracene with Na-D₂O/THF. A similar reduction of anthracene-d₁₀ [**1b**] readily gave **2b**. Infrared analysis of **2a** indicated that deuterium incorporation was limited to positions 9 and 10 since carbon-deuterium bond stretching was observed in the aliphatic (1900-2100 cm⁻¹) and not the aromatic region (2100-2205 cm⁻¹). Results from NMR studies shown in Table I indicate the extent of deuterium incorporation for **2a** and **2b** and the absence of deuterium in the outer rings of **2a**.

Table I. Incorporation of Deuterium at C-9 and C-10 of **2a** and **2b**.

Compound	mol Fraction ^a		%d
	d ₁	d ₂	
2a	0.22	0.78	89
2b	0.05	0.95	97

^aThese data were obtained, as presented in the Experimental Section, through use of ¹H - and ¹³C-NMR studies.

The reducing system (Na - H₂O/THF or Na - D₂O/THF) should prove useful in other applications.

EXPERIMENTAL SECTION

9,10-Dihydro-9,9,10,10-d₄-anthracene (2a). A dry, (4) 500-mL, three-neck, round-bottom flask fitted with a reflux condenser, additional funnel and Teflon-coated magnetic stirring bar was conditioned internally by adding 25 mL of D₂O (5) in a dry argon (6) atmosphere and then heated at reflux for 6 h. The spent D₂O was removed and the process was repeated. Dry THF (7) (250 mL) and 14.8 g of **1a** were then added to the reaction flask. During 8 h, 18 g of sodium (8) and 30 mL of deuterium oxide (5) were added portionwise to the refluxing reaction mixture. Reflux was continued until all the sodium had reacted. The reaction mixture was poured onto an ice-water slurry and extracted with ether. The ether layer was dried (MgSO₄), filtered and concentrated. The resulting solid was dissolved in hexane and passed through a column containing single layers of silica-gel and acidic and basic alumina. Kugelrohr distillation gave 7.0 g (94%) of colorless solid **2a**; ¹H - NMR (9a) (CDCl₃, 9.0% wt.) δ 7.23 (4, m, ArH), 7.15 (4, m, ArH), 3.85 (s, residual ArCH₂ Ar). Comparison of the integral of this latter peak with that of undeuterated material indicated that 89% of the 9,10-positions of **2a** were deuterated; ¹³C-NMR (9b) (CDCl₃, 9.0% wt.) 136.6, 127.3, 126.0, 36.0, 35.9, 35.7, 35.4, 35.1, 34.8 ppm. The ¹³C-NMR spectrum in the region 34-37 ppm was interpreted qualitatively

as an overlapping 1,1,1-triplet and a 1,2,3,2,1-quintuplet with the center shielded 0.35 ppm. Both multiplets showed $J_{CD} = 19.6$ Hz. The triplet arises from ArCDHAr and the quintuplet from ArCD₂Ar coupling. Comparison of the integrals of individual peaks in this region (10) showed that 78% of the 9,10-carbons were completely deuterated with the remainder monodeuterated.

9,10-Dihydro-9,10-d₂-anthracene-d₁₀ [2b]. A 4.7 g sample of commercial 1b (98+% D), in 50 mL of dry THF, was treated as above with 10 mL of D₂O (5) and 4 g of sodium (8) to give 4.8 g of colorless solid 2b; ¹H-NMR (9a) (CDCl₃ 6.9% wt.) δ 7.25 (s, residual ArH), 7.16 (s, residual ArH), 3.88 (m, residual ArCH₂Ar). The residual peak areas indicated that the 1,4- and 2,3-ArH positions had about one-half the protonation at the 9,10 positions; ¹³C-NMR (9b) (CDCl₃, 6.9%) 136.5, 126.9 (m, ArD), 125.5 (m, ArD), 35.8, 35.6, 35.3, 35.0, 34.7 ppm. The aromatic region showed 1,1,1-triplets ($J_{CD} = 24.1$ Hz) arising from ArD. Again, the pattern in the 34-37 ppm was interpreted as an overlapping 1,1,1-triplet and a 1,2,3,2,1-quintuplet with the quintuplet center shielded 0.35 ppm ($J_{CD} = 19.6$ Hz). The integrals of the peaks (10) showed that 95% of the 9,10-carbons were completely deuterated, with the remainder monodeuterated. Because there were twice as many equivalent carbons representing each of the aromatic peaks and there was approximately one-half the protonation at the 1,4- or 2,3-positions, about 1.2 mol % of the aromatic positions were undeuterated.

2b; 8K points for 2a, 16 K points for 2b (zero-filled once); acquisition time - 1,437 s (2a), 2,874 s (2b); pulse delay - 3.0 s (2a), 5.0 s (2b); quadrature phase detection.

9. (b) This instrument was operated at 67.9 MHz for ¹³C-NMR, and TMS was used in all studies as internal standard; spectral width - 10706.6 Hz; filter bandwidth - 5350 Hz, pulse length - 8.0 μs 45 degree, 16K points (zero-filled once for 2b); acquisition time - 0.765 s; pulse delay - 60 s; quadrature phase detection.

10. These data were obtained from a gated-decoupling experiment with 45° pulse and 60 s pulse delay to achieve quantitative results.

ACKNOWLEDGEMENT

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- All glassware was heated at 165 °C for 48 h, assembled hot and allowed to cool under a flow of dry argon.
- Deuterium oxide, 99.8% was used.
- Argon was passed through Molecular Sieves previously dried overnight at 250 °C/0.1 mm.
- THF was refluxed with the sodium for 12 h and was then distilled directly into the dry reaction flask.
- A glove bag containing argon was used to protect sodium during cutting. The sodium pieces subsequently were placed in a screw-cap vial and this vial was attached to the reaction flask, for dispensing, through a short length of dry Gooch tubing.
- (a) ¹H-NMR spectra were recorded at 270.17 MHz using a JEOL GX 270/89 instrument. TMS was used as the internal standard; spectral width 2850.6 Hz; filter bandwidth - 1450 Hz; pulse length - 19.2 μs (78 degree) for **2a**, 11.1 μs (45 degree) for