

PERDEUTEROBENZENE⁺

Richard A. Russell and Ronald N. Warrener
Department of Chemistry, S.G.S. Australian National University,
Canberra, A.C.T., 2600, Australia
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SUMMARY

2-Aminobenzoic acid-3,4,5,6-²H₄ was prepared from the protic acid by a platinum catalysed exchange reaction in deuterium oxide. The deuterated acid provided a source of perdeuterobenzene which was trapped with selected dienes.

Key Words: Benzene, catalytic exchange, deuterium, ²H.n.m.r.

INTRODUCTION

In view of the widespread use of benzyne as a reactive intermediate, it is surprising that a method of generating benzyne-²H₄ has not been reported.

As aniline-²H₅ had previously been described^{2,3}, we initially considered generating benzyne-²H₄ by the reaction of aniline-²H₅ with 4-chlorobenzoyl nitrite⁴. However, this reaction proved to be a poor source of benzyne for a number of cycloaddition reactions¹. Accordingly we examined the more generally applicable method of Friedman⁵, which generates benzyne from 2-aminobenzoic acid and isopentyl nitrite. An extension of this work to the current problem clearly required a facile preparation of 2-aminobenzoic acid-3,4,5,6-²H₄. Two previous studies involving benzoic acids^{2,6} suggested that this could be achieved by the catalytic exchange of protium in 2-aminobenzoic acid for the deuterium in deuterium oxide. In practice this was best achieved by the equilibration of potassium 2-aminobenzoate with deuterium oxide in the presence of platinum. Deuterium analysis of the product from one such equilibration + Perdeuterobenzene is predominantly benzyne-²H₄ but contains a small quantity of benzyne-3,4,5-²H₄.

revealed a deuterium content of 91% in the aromatic ring. A second equilibration of this material raised the figure to 97%. The ^1H and ^2H n.m.r. spectra of this product indicated that residual protium was largely centered at the 6 position.

Benzynes generated from deuterated 2-aminobenzoic acid was trapped with 2,3,4,5-tetraphenylcyclopenta-2,4-dienone and 6,6-dimethylfulvene. The products, 1,2,3,4-tetraphenyl-naphthalene⁵ and 1,4-dihydro-9-(1-methylethylidene)-1,4-methano-naphthalene⁷, were analysed for deuterium and in both cases the extent of deuteration was identical to that of the 2-aminobenzoic acid used to generate the benzyne. Furthermore ^1H -n.m.r. confirmed that the deuterium was located in the expected positions.

EXPERIMENTAL

Melting points are uncorrected and were recorded on a Richert hot-stage. ^1H -n.m.r. spectra were recorded on a Jeolco Minimar 100 MHz spectrometer; added tetramethylsilane was used as an internal standard and resonances are quoted in $^1\text{H}\delta$ units. ^2H -n.m.r. were recorded at a frequency of 41.4 MHz by the National N.M.R. Centre, Canberra, A.C.T. Resonances are reported on the $^2\text{H}\delta$ scale and are relative to cyclohexane- $^2\text{H}_{12}$, which was used as an internal reference. Mass spectra were measured at 15 eV., on a Varian MAT CH7 mass spectrometer. Ion intensities are corrected for natural isotopic abundance.

2-Aminobenzoic acid-3,4,5,6- $^2\text{H}_4$

2-Aminobenzoic acid (1.37 g) was suspended in water (20 ml) and neutralised with potassium carbonate (1.40 g). The solvent was removed and the residue dried in vacuo ($40^\circ/0.1$ mm) for 24 hours. Potassium 2-aminobenzoate (1.0 g) was dissolved in deuterium oxide (5 ml, 98% ^2H) and the solution mixed with platinum which had previously been prepared by the reduction of platinum(IV) oxide (0.1 g) with deuterium. The mixture was sealed in a heavy walled glass tube and heated at 130° in a rocking furnace for 48 hours. When cool, the tube was opened and its contents filtered twice through cellulose powder. The

The filtrates and washings were chilled at 5° and the pH adjusted to 5 by careful addition of glacial acetic acid. The crude product was collected by filtration and recrystallised twice from water to yield light brown needles (0.34 g 43%), m.p. 145-146° (lit⁸ 144-146°). ²H-n.m.r. spectrum (acetone): δ 5.30 (1²H, s, Ar-²H5), 5.50 (1²H, s, Ar-²H3), 5.96 (1²H, s, Ar-²H4), 6.55 (1²H, s, Ar-²H6); Mass spectrum: m/e (rel. intensity): 141(10), 140(4.8). This corresponds to 91% deuterium incorporation with the ²H₄:²H₃ ratio of 1:0.48. 2-Aminobenzoic acid which had been subjected to two such equilibrations was shown to have a 97% deuterium incorporation with a ²H₄:²H₃ ratio of 1:0.15. Large scale preparations were conveniently conducted in a pressure bottle.

Trapping of benzyne-²H₄ with 2,3,4,5-tetraphenylcyclopenta-2,4-dienone

2,3,4,5-Tetraphenylcyclopenta-2,4-dienone (0.384 g) was dissolved in refluxing dioxan (5 ml). Solutions of 2-aminobenzoic acid-²H₄ (0.164 g) in dioxan (2 ml) and isopentyl nitrite (0.2 ml) in dioxan (2 ml) were simultaneously dropped into the solution of the dienone, over a period of 20 minutes. The solution was cooled and the solvent removed to yield an orange oil which crystallised when triturated with ethanol (2 ml). The crude product was recrystallised from a mixture of benzene and ethanol, and finally sublimed (150°/0.01 mm) to yield colourless crystals of 1,2,3,4-tetraphenylnaphthalene-5,6,7,8-²H₄ m.p. 203-204° (lit⁵ 203°). ¹H-n.m.r. spectrum (CDCl₃): δ 6.90 (1OH, s, PhH), 7.26 (1OH, s, PhH).

Trapping of benzyne-²H₄ with 6,6-dimethylfulvene

This experiment was conducted according to the method of Watson and Warrener⁷. The product, 1,4-dihydro-9-(methylethylidene)-1,4-methanonaphthalene-5,6,7,8-²H₄ was recrystallised from ethanol, m.p. 92° (lit⁷ 92°). ¹H-n.m.r. spectrum (CDCl₃): 1.54 (6H, s, CH₃), 4.42 (2H, t, C 1,4 H), 6.92 (2H, t, C 2,3 H). The mass spectrum revealed that the deuterium content of the product was identical to that of the 2-aminobenzoic acid used to generate the benzyne.

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