

Synthesis of deuterated decalin

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A volume of approximately 30 gallons of high purity decalin in which more than half of the H atoms overall were replaced by D was required as a scintillator solvent in studies of the antineutrino reaction. The stereochemistry of the decalin was of no importance in the intended use.⁽¹⁾ The desired product was prepared by the Pt catalyzed reduction of naphthalene with D_2 gas under conditions developed to minimize waste of costly D_2 and to ensure completeness of the reaction, since naphthalene and tetralin are not conveniently and cleanly separable from decalin in volumes of this size.

The requisite amount of decalin- D_{9+} was the combined product of twelve individual batches each prepared in the following way. A 5-gallon stainless steel autoclave was heated to about 80°C to melt 7.5 kg of naphthalene (<10 ppm S content), 5.5 liters of $\text{CH}_3\text{CO}_2\text{D}$,⁽²⁾ prepared by hydrolysis of acetic anhydride by D_2O , was added, then 120 g of PtO_2 hydrate (Adams catalyst). The autoclave was sealed, purged with N_2 , then pressured with D_2 to 40 atmospheres. Agitation was achieved with a "Dispersimax"⁽³⁾ hollow shaft gas dispersing impeller and baffle; use of a common screw-type impeller resulted in the formation of tetralin as the main product. The temperature of the batch rose very rapidly without external heating and was controlled at about 125°C by immersed cooling coils throughout the run. Pressure of D_2 was maintained at about 40 atmospheres, but occasionally fell as low as 16 atmospheres either to permit more complete removal of D_2 from the storage cylinders or, in some instances, when the feed lines could not accommodate sufficient gas to replace that being consumed in the reaction. In any event, pressure toward the conclusion of the run was restored to 40 atmospheres, and the temperature was allowed to rise to 155°C and maintained at that value by external heating for 30 minutes to complete the reaction. From first introduction of the D_2 gas, the entire reaction period was about one hour.

After cooling the reaction mixture, D_2 in the head space was removed by mercury piston displacement and recompressed for use in subsequent runs. The product was filtered to remove catalyst and the two liquid phases were separated and distilled separately. The upper phase was distilled through a 125 cm packed column at 140 mm pressure, and the product was collected at $126\text{-}129^\circ\text{C}$. Forerun $\text{CH}_3\text{CO}_2\text{D}$ was used as solvent for subsequent runs, and an intermediate mixed fraction was added to a subsequent distillation batch. The lower phase was treated with 90% of the amount of acetic anhydride needed to react with the water introduced by the hydrated catalyst and the D_2O formed by reduction of PtO_2 to Pt. Small amounts of free acetic anhydride or somewhat larger amounts of free water present in the reaction

solvent caused appreciable tetralin formation. $\text{CH}_3\text{CO}_2\text{D}$ was then distilled at atmospheric pressure from the lower phase and recovered for reuse, and the higher boiling residue was added, without distillation, to the next upper phase distillation batch.

Recovered catalyst showed reduced activity. The platinum from each run was washed successively with several portions each of acetone, water, acetic acid and ethanol in that sequence and finally with acetone again. To the catalyst recovered from each run, 40 g of fresh PtO_2 hydrate was added for the succeeding run. In spite of this incremental addition of new catalyst, the last few runs required somewhat longer reaction periods than the first few.

The product consisted of approximately 15 per cent trans- and 85 per cent cis-decalin as determined by gas phase partition chromatography using silicone DC-710 on 60-80 mesh firebrick as the stationary phase.⁽⁴⁾ No tetralin, naphthalene, or acetic acid could be detected by this method. The first two of these possible contaminants should be detected if present individually in amounts as small as 0.05 percent. The chromatographic method is less sensitive for acetic acid which was also sought by infrared absorption (carbonyl bond). As little as 0.02 percent of acetic acid could be detected in this way and none was found.

The deuterium content of the product was determined in three ways. Carbon analysis produced values of 81.0, 81.1, and 81.0 percent carbon. The calculated value for $\text{C}_{10}\text{H}_8\text{D}_{10}$ is 81.1 percent, and that for $\text{C}_{10}\text{H}_9\text{D}_9$ is 81.6 percent. Nuclear magnetic resonance spectroscopy gave a value of ≤ 5.85 percent hydrogen content. This is equivalent to a compound of average composition $\text{C}_{10}\text{H}_{8.6}\text{D}_{9.4}$ or better, i.e., higher in deuterium content. Mass spectrometry indicated the average composition to be $\text{C}_{10}\text{H}_8\text{D}_{10}$ and showed the following distribution of deuterated species indicative of the random distribution to be expected under the conditions (catalyst, temperature) used, due to exchange.

No. of D Atoms	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Percent	0.2	0.7	1.9	4.4	8.1	11.9	15.0	16.0	14.5	12.0	8.2	4.4	1.9	0.5	0.2

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