Deuterated Organic Compounds XXV Synthesis of certain Deuterated n-Undecanes and n-Dodecanes *

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SUMMARY

The synthesis of the following n-undecanes and n-dodecanes deuterated in specific positions is described : $CH_3(CH_2)_{10}CD_3$, $CD_3(CH_2)_{10}CD_3$, $CH_3(CD_2)_{10}CH_3$, $[CD_3(CD_2)_4CH_2]_2$, $[CD_3(CD_2)_4]_2CH_2$, $CD_3(CD_2)_3(CH_2)_3$ $(CD_2)_3CD_3$, and $CD_3(CD_2)_3CH_2CD_2CH_2(CD_2)_3CD_3$. The following new intermediates were prepared in the course of these syntheses : $CCl_3CD_2CD = CDCD_2CN$, $CCl_3CD_2CD = CDCD_2CO_2H$, $CCl_3CD_2CD = CDCD_2CO_2C_2H_5$, $CCl_3(CD_2)_4CO_2C_2H_5$, $CH_3(CD_2)_4CO_2C_2H_5$, $CD_3(CD_2)_4CO_2C_2H_5$, $CH_3(CD_2)_4CO_2C_2H_5$, $CH_3(CD_2)_4CD_2OH$, $CH_3(CD)_4C_2D_2Br$, $CD_3(CD_2)_4CO_2D$, $[CD_3(CD_2)_4]_2CO$, $[CD_3(CD_2)_4]_2CHOH$, $[CD_3(CD_2)_4]_2CHBr$, $[CD_3(CD_2)_3CH_2]_2CO$, $[CD_3(CD_2)_3CH_2]_2CDOH$, $[CD_3(CD_2)_3CH_2]_2CDBr$, $[CD_3(CD_2)_3CH_2]_2CHOH$, $[CD_3(CD_2)_3CH_2]_2CHBr$.

In connection with an intensive examination of the vibrations of the methylene group in the Raman and infrared to be reported by JONES and SHEPPARD [1] the deuterated n-undecanes and n-dodecanes shown below were synthesized :

$CH_3(CH_2)_{10}CD_3$	I	$[CD_3(CD_2)_4]_2CH_2$	V
$CD_3(CH_2)_{10}CD_3$	II	$CD_3(CD_2)_3(CH_2)_3(CD_2)_3CD_3$	VI
$CH_3(CD_2)_{10}CH_3$	III	$CD_3(CD_2)_3CH_2CD_2CH_2(CD_2)_3CD_3$	VII
$[CD_3(CD_2)_4CH_2]_2$	IV		

Compound I was prepared in four steps by well-known reactions from methyl laurate. Reduction of the ester with lithium aluminium deuteride led

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to lauryl alcohol labelled on the end carbon atom. The alcohol was converted into the bromide by the action of hydrobromic and sulphuric acids. Reductive debromination of the bromide with zinc dust in alkaline deuterium oxide gave the desired compound. The experience gained in carrying out the reactions just described was valuable in the preparation of II. Methyl 12,12,12-trichloro-laurate prepared as described by ISABELLE and LEITCH [2] was subjected to reductive dechlorination to give methyl 12,12,12-trideuteriolaurate. n-Dodecane labelled on both methyl groups was prepared from this compound by the reactions which gave rise to I.

The remaining compounds in the series were all synthesized from hexadeuteriobutadiene. The preparation of this deuterated hydrocarbon was first reported by one of us in 1956 [3]. Somewhat later, PICHAT and CHATE-LAIN [4] described the preparation of hexadeuteriobutadiene by the same method and its purification by Ilosvay's reagent followed by chromatography on celite impregnated with dimethylformamide. The yield of pure butadiene was 60 % based on hexachlorobutadiene. The mass spectrum of our product was not scanned for masses below 55. The peak at mass 56 of intensity 44.4 (relative to 376 for the parent mass 60) was attributed to loss of two deuterium atoms. Actually, this peak was due, wholly or partly at least, to vinylacetylene present in our sample. Still more recently, CRAIG and FOWLER [5] estimated the acetylenic impurities in the crude butadiene prepared by our method by measuring the percentage of product which reacted with maleic anhydride. These authors found that the yield of pure butadiene could be improved by carrying out the dechlorination in deuterium oxide which contained 0.5 % of dissolved sodium iodide and 3 % of cupric chloride. The deuteriobutadiene employed in the present work was always prepared by this simplified method rather than in deuterium oxide-dioxane and used without purification to prepare trans-1,1,1-trichloro-5-bromohexadeuteriopentene-3 by addition of bromotrichloromethane under free radical conditions as earlier reported by us [6]. PYNE [7] recently prepared the normal halopentene by the same method, apparently unaware of our publication. In addition to earlier evidence for the formation of a single product in this reaction, the vapor phase chromatogram shows only one band. The bromide was converted into the cyanide by the action of cuprous cyanide in acetonitrile. The vapor phase chromatogram of the product likewise showed only one band.

The hydrolysis of the nitrile was carried out in deuteriobromic acid. When ordinary 48 % hydrobromic acid was used for hyd rolysis, deuterium on the carbon atom adjacent to the nitrile group was partly lost by exchange as judged by the NMR spectrum of the product. The trichlorodeuteriopentenoic acid obtained was a mixture of cis and trans forms which could be readily separated by fractional distillation under reduced pressure. One of the isomers is a solid, m. 67-8°, presumably the trans form. Since the double bond is reduced at a later stage it is unnecessary to separate the isomers before esterification of the acid.

For the synthesis of eicosadeuteriododecane (III) the unsaturated ester was reduced selectively with deuterium and platinum black to ethyl 6,6,6-trichlorooctadeuteriohexanoate. Reductive dechlorination with zinc dust in acetic acid afforded ethyl 2,3,4,5-octadeuteriohexanoate. The ester was then reduced to 2,3,4,5,6-decadeuteriohexyl alcohol with LiAlD$_4$. The bromide was obtained by heating the alcohol with a mixture of hydrobromic and sulphuric acids. The Würtz synthesis carried out with the deteurated n-hexyl bromide finally gave the deuterated n-dodecane III.

To synthesize the dodecane IV labelled with deuterium everywhere except in two central methylene groups, ethyl 6,6,6-trichlorohexadeuterio-3-hexenoate was reduced and dechlorinated in one step with deuterium and palladium in the presence of magnesium oxide to ethyl perdeuteriohexanoate. The remaining steps to IV were the same as those for III.

Ethyl perdeuteriohexanoate could also be prepared by the desulphurizing deuteration reaction explored by BUU-HOÏ, XUONG and BAC [8] from 5-methyl-2-acetylthiophene. In this connection, the platinum-catalyzed deuterium oxide exchange of thiophene was examined. After two exchanges at 140° almost 80 % of the hydrogen had been exchanged for deuterium. 2-Methylthiophene-5- carboxylic acid could probably be converted into the totally deuterated compound in the same manner. However, this route to ethyl perdeuteriohexanoate turns out to be just as long as that from hexa-deuteriobutadiene.

Compounds V, VI and VII of the series were also prepared from ethyl perdeuteriohexanoate. The ester was hydrolyzed to the acid which was converted into n-undecanone in good yield when heated with iron powder [9]. The ketone was exchanged several times with alkaline deuterium oxide to replace the residual hydrogen adjacent to the carbonyl group. It was then reduced to the alcohol with lithium aluminum hydride. The bromide was prepared from the alcohol and dehydrobrominated with zinc and euterium oxide to V.

The compounds VI and VII were prepared from n-undecanone which had been exchanged with alkaline water to remove deuterium adjacent to the carbonyl group. The carbonyl group was then converted into CH$_2$ or CD$_2$ as described for compound V.

The deuterium content of compounds I and II was determined by combustion according to the procedure of MACKENZIE and JONES [10].

The deuterium content of compounds III to VII as determined by the mass analyses reported in the experimental part appears at first sight to be unduly low considering the deuterium oxide used was 99.6 mol % D. For example, compound V contains 66.4 % D$_{20}$, 27.0 mol % D$_{19}$ and 5.5 mol % D$_{18}$. In terms of atom %, however, the deuterium content comes to 97.2 % which is surprisingly high considering there are ten steps in the synthesis and there is a chance of contamination with ordinary water at each stage from adsorbed water on the apparatus, slight exchange during working up operations in aqueous or alcoholic media, etc.

There are also theoretical reasons why the deuterium content of the final products cannot possibly be as high as that of the deuterium oxide employed. Consider, for example, the reaction $CCl_4 + D_2O \rightarrow CD_4 + DCl$ which takes place in deuterium oxide in the presence of excess zinc dust. The dechlorination actually occurs in four steps; so, if the mole fraction of deuterium oxide is x, then the mole fraction of CD_4 in the product is expressed by x^4, the mole fraction of CHD_3 is given by $3x^3 (1-x)$ and so on. If $x = 0.996$ then $n^4 = 0.984$ which means that the CD_4 content of the deuterated methane cannot exceed 98.4 mol %; nearly all the rest of the deuterated methane, i.e. 1.19 % will be CHD_3. In this discussion hydrogen isotope effects are assumed to be absent. As the number of deuterium atoms in the molecule increases the effect of protium in the D_2O becomes more important. For compound V, $C_{12}D_{22}H_2$, the maximum deuterium content in mol % with deuterium oxide of varying isotopic purity is shown in the following table :

Mole % D_2O	Mole % D_{22}	Mole % D_{21}
99.6	92.0	7.7
99.0	80.2	19.1
98.0	64.1	27.5
96.0	40.7	35.6
90.0	9.9	43.0

The observed deuterium content of V would indicate that the isotopic purity of the water employed had been reduced to slightly over 98 % by the factors considered above.

EXPERIMENTAL

DEUTERIATED DODECANES.

1,1-Dideuterio-n-dodecanol.

A solution of methyl laurate (10.7 g; 0.1 mole) in 60 ml of absolute ether was added dropwise to a stirred solution of lithium aluminum deuteride (3.0 g; 0.07 mole) in 150 ml of absolute ether in a 500 ml round bottomed flask equipped with a reflux condenser and a drying tube. The quantity of deuteride specified is the minimum amount that can be used without precipitation of a complex before all the ester has been added. After having stirred the reaction mixture for 3 hours under reflux, 50 ml of 3N hydrochloric acid was added and the ether layer was separated in a funnel. It was washed with water and dried over anhydrous potassium carbonate. Bulb-to-bulb distillation of the residue after removal of solvent yielded 8.5 g of the alcohol which solidified on standing. Yield : 90 %.

1,1-Dideuterio-n-dedecyl Bromide.

The alcohol (8.5 g; 0.046 mole) was heated under reflux for four hours with 15 g of 48 % hydrobromic acid and 4.0 ml of 95 % sulphuric acid. The lower layer of acid was separated in a funnel and the halide dissolved in pentane was washed with water and dried over calcium chloride. Bulb-to-bulb distillation (Späth tube) under .01 mm pressure gave 8.5 g of product (80 % yield).

1,1,1-Trideuterio-n-dodecane.

A Grignard reagent was prepared from magnesium turnings (0.9 g) and the above bromide in 50 ml of absolute ether. It was then decomposed by adding 5.0 ml of deuterium oxide. The ether solution was decanted, filtered and dried. The residue from the ether was distilled under .01 mm in a Späth bulb. It gave two fractions; the first, b.p. 60°, was the desired dodecane, n_D^{20} 1.4200 and amounted to 3.0 g. The second fraction came over at 125-130° and solidified in the cold bulb. Yield : 1.5 g. This product is probably produced by coupling between the Grignard reagent and the halide. It was identified by its m.p. as tetracosane, m.p. 51°.

Alternatively, the bromododecane was converted by reductive debromination with zinc dust in anhydrous dioxane and deuterium oxide. The yields were slightly lower, however, and the product occasionally contained unreacted bromododecane as shown by a positive Beilstein test. In this case the product was purified by allowing it to stand over sodium and then distilling it in a Späth bulb under .01 mm.

1,1,12,12,12-Pentadeuteriododecanol.

Methyl 12,12,12-trideuteriododecanoate, prepared as described by ISABELLE and LEITCH [2], was reduced with lithium aluminum deuteride exactly as described above for the normal compound. The yield of product, n_D^{22} 1.4430, was similar.

1,1,12,12,12-Pentadeuteriododecyl Bromide.

The above alcohol was converted into the bromide as described above for the dideuterio compound in 70 % yield. n^{20} 1.4578.

1,1,1,12,12,12-Hexadeuteriododecane.

The above bromide was debrominated as described above for the dideuteriocompound. n_D^{20} 1.4200.

Hexadeuteriobutadiene-1,3.

Following the procedure of CRAIG and FOWLER [5], hexachlorobutadiene (65 g; 0.25 mole) was added with constant stirring over a period of 4 hrs. to a boiling suspension of 120 g of zinc dust, 1.0 g sodium iodide and 7.6 g

cupric chloride dideuterate in 200 ml of deuterium oxide. The deuterated butadiene was condensed in a spiral trap cooled to —78° with dry-ice and acetone. The crude product was redistilled into another tared trap. Yield : 11.9 (80 %).

Mass analysis : C_4D_6,   92.6 %
$\qquad\qquad\qquad$ C_4D_5H,   6.9
$\qquad\qquad\qquad$ $C_4D_4H_2$,   0.5

Atom % D : 98.7.

The yields in six preparations were consistently 80 to 85 %.

5,5,5-Trichloro-1-bromo-hexadeuteriopentene-2.

Hexadeuteriobutadiene-1,3 (24.0 g; 0.4 mole) was distilled under vacuum into a quartz flask which contained 250 ml of freshly-distilled bromotrichloromethane. The flask was stirred and irradiated with UV light for 12 hrs. at atmospheric pressure. Excess bromotrichloromethane was distilled off under reduced pressure and the residue was purified by distillation under 0.05 mm pressure in a Späth bulb immersed in an air bath heated to 50-60°. The yield of product, n_D^{20} 1.5325, was 94.0 g (91 %).

5,5,5-Trichloro-1-cyano-hexadeuteriopentene-2.

The bromochloropentene prepared above (94 g; 0.37 mole) was added dropwise over a period of one hour to a stirred boiling suspension of 42.8 of cuprous cyanide in 230 ml of acetonitrile. The reaction mixture was heated under reflux with stirring for 4 hrs., cooled and filtered. Most of the solvent was distilled off under reduced pressure. The residue was taken up in 300 ml of ether and filtered from insoluble cuprous bromide. The oil recovered from the ether solution was distilled in a Späth bulb from an air bath at 60-70°. The yield of product, n_D^{20} 1.4962, was 62 g or 84 % of the theoretical amount. For the normal nitrile, n_D^{20} 1.4971, the vapor phase chromatogram on an « 0 » column of a Perkin Elmer Fractometer gave only one band.

6,6,6-Trichloro-2-hexenoic Acid.

A mixture of 30 g (0.15 mole) of 5,5,5-trichloro-2-pentenonitrile, 45 ml acetic acid and 25 ml 48 % hydrobromic acid was heated under reflux for 24 hrs. The cold reaction mixture was poured into water (200 ml) and the oil was taken up in ether (100 ml). The ether layer was washed several times with water and dried over a little calcium chloride. The residue obtained after having removed the solvent was distilled under reduced pressure in a flask with a short Vigreux column. The main fraction was a liquid, b.p. 136°/.05 mm., n_D^{20} 1.5150. It was followed by a second fraction, b.p. 136-145°/.05 mm which solidified to a solid, m.p. 67-8° after recrystallization from pentane. The total yield was 24.6 g or 75 % of the theoretical amount. The neutralization equivalent of each fraction was determined and

found to be 219 and 220. The two fractions are obviously geometrical isomers. It appears that the precursors of the acid, the nitrile and the bromo compound are mixtures of *cis* and *trans* isomers with the latter predominating since the trans form of such acids always has the higher m.p.

6,6,6-Trichlorohexadeuterio-2-hexenoic Acid.

The deuterionitrile (31.5 g; 0.15 mole) was hydrolyzed as described above. The yield of acid obtained by distillation in a Späth bulb was 31.0 g (90 %), n_D^{20} 1.5092. It was a mixture of the *cis* and *trans* forms. The NMR spectrum showed the presence of protons on the carbon atom adjacent to the carboxyl group. To avoid loss of deuterium by exchange with the solvent subsequent hydrolyses were carried out in deuterium bromide-deuterium oxide solution. For example, 50 ml deuterium oxide and 61.8 g of the nitrile were saturated with deuterium bromide from a cylinder. The mixture was stirred and heated at 80° overnight. In the morning the reaction mixture was again saturated with deuterium bromide and heated for a day. The organic acid was dissolved in 300 ml of ether and the solution was washed with water. Distillation of the residue from the ether in a Späth bulb under 0.05 mm gave 57.0 (90 %) of mixed acids.

Ethyl 6,6,6-Trichlorohexadeuterio-2-hexenoate.

The mixture of the above acids (31 g; 0.135 mole) was esterified in 175 ml of absolute ethanol using 3 ml concentrated sulphuric acid as a catalyst. The ester was worked up in the usual manner and distilled in a Späth bulb. Yield : 30.5 g (87.4 %), n_D^{20} 1.4842.

6,6,6-Trichloroöctadeuteriohexanoate.

Ethyl 6,6,6-trichlorohexadeuterio-2-hexenoate (30.4 g; 0.12 mole) was reduced in 30 ml of C_2H_5OD with deuterium in the presence of 0.3 g of platinum oxide. The pressure in the tank fell 26 lbs. in slightly less than nine hours. The alcohol was removed under vacuum and the ester was distilled in a Späth bulb. Yield : 24.3 g of saturated ester, n_D^{20} 1.4651.

Ethyl 2,2,3,3,4,4,5,5-octadeuterio-n-hexanoate, $CH_3(CD_2)_4CO_2C_2H_5$.

The above trichloro ester (23.2 g; 0.09 mole) was dissolved in 115 ml of acetic acid and 35 g of zinc dust were added in small portions at ten minute intervals while stirring. After heating for 18 hours under reflux the reductive dechlorination was complete and the reaction mixture was poured onto ice. The oil was taken up in ether and the ether solution was washed and dried with a little calcium chloride. The residue from the evaporation of the ether was distilled on the vacuum line. Yield : 12.1 g (87.3 %), n_D^{20} 1.4046.

1,1,2,2,3,3,4,4,5,5-Decadeuteriohexanol, $CH_3(CD_2)_4CD_2OH$.

To 4.35 g of lithium aluminum deuteride in 225 ml absolute ether in a 500 ml 2-necked round-bottomed flask were added 11.4 g (0.075 mole) of

ethyl 2,2,3,3,4,4,5,5-octadeuteriohexanoate over a period of 1 hr. The solution was stirred at the ambient temperature for 20 hrs. The flask was then immersed in ice water and excess hydride and complex were decomposed by adding carefully 120 ml of 10 % sulphuric acid. The ether solution was separated, washed with water, dried over potassium carbonate and freed of solvent on the steam bath. The residue was distilled in a Späth bulb. Yield : 7.7 g (92 %), n_D^{20} 1.4100.

1,1,2,2,3,3,4,4,5,5-Decadeuteriohexyl Bromide.

The alcohol obtained above was stirred at 90° for 17 hrs. with 26.4 g of 48 % hydrobromic acid and 8 g of concentrated sulphuric acid. The oil in the cold reaction misture was taken up in pentane and the solution was washed three times with concentrated sulphuric acid to remove unchanged alcohol. It was finally washed with water and dried over calcium chloride. The pentane was distilled off and the residue was distilled in a Späth bulb under reduced pressure. Yield : 9.8 g (82 %), n^{20} 1.4427. For the normal bromide, n_D^{20} 1.4478.

1,1,1,12,12,12-Protiodeuteriododecane [1], $CH_3(CD_2)_{10}CH_3$ (III).

The halide from the last preparation was added dropwise to sodium cut in small pieces in a flask equipped with a separatory funnel and a condenser. An exothermic reaction set in after each addition of bromide. The reaction mixture was allowed to stand one hour and 2.5 ml of ethanol were added to destroy unreacted sodium. The reaction mixture was extracted with ether and washed with water. The residue from the evaporated ether was distilled in a Späth bulb under reduced pressure. Yield : 4.0 g (80 %), n_D^{20} 1.4170.

Mass analysis : $C_{12}D_{20}H_6$,   60.7 %
$\qquad\qquad\qquad\; C_{12}D_{19}H_7$,   29.6
$\qquad\qquad\qquad\; C_{12}D_{18}H_8$,   7.1
Analysis on atom % basis : 97.2 %.

Ethyl Perdeuteriohexanoate, $CD_3(CD_2)_4CO_2C_2H_5$.

Ethyl 6,6,6-trichlorohexadeuterio-2-hexenoate (17.5 g; 0.07 mol) was shaken in 100 ml deuterium oxide with 8.2 g of palladium-barium sulphate catalyst and 10.8 g of magnesium oxide under 56 lbs. of deuterium. After 24 hrs. the pressure in the tank remained constant. The reaction mixture was diluted with 300 ml of water, acidified with 10 % nitric acid and extracted with ether. The residue from the ether was distilled in a Späth bulb under reduced pressure. Yield : 8.2 g (76.2 %), n_D^{20} 1.4039.

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[1] This nomenclature appeared simplest for naming compounds which contain a large number of deuterium atoms and few hydrogen atoms.

2,2,3,3,4,4,5,5,6,6,6-Undecadeuteriohexyl Alcohol, $CD_3(CD_2)_4CH_2OH$.

The reduction of the aforementioned ester was carried out with $LiAlH_4$ exactly as described in the case of the completely deuterated alcohol. Yield : (from 8.0 g of ester) : 5.5 g (93.5 %), n_D^{20} 1.4121.

2,2,3,3,4,4,5,5,6,6,6-Undecadeuteriohexyl Bromide, $CD_3(CD_2)_4CH_2Br$.

The bromide was prepared from the alcohol (5.3 g) as described above for the completely deuterated compound. Yield : 7.4 g (90 %), n_D^{20} 1.4420.

6,6,7,7-Tetraprotiodeuteriododecane (IV).

The Würtz synthesis was carried out as already described. Yield : 2.6 g from 7.2 g of bromide (67 %), n_D^{20} 1.4170.

Mass analysis : $C_{12}D_{22}H_4$,   65.0 %
                 $C_{12}D_{21}H_5$,   27.1 %
                 $C_{12}D_{20}H_6$,   6.0 %
Atom % D : 97.9.

DEUTERIATED UNDECANES.

Eicosadeuteriohexanoic Acid, $CD_3(CD_2)_4CO_2D$.

Ethyl eicosadeuteriohexanoate (12.0 g; 0.085 mol) was hydrolyzed in 100 ml of deuterium oxide which contained 12 g of dissolved sodium deuteroxide. The base was prepared by adding sodium in small portions to the deuterium oxide under an inert atmosphere. The solution of sodium salt was acidified with deuteriosulphuric acid prepared as in reference [6]. The yield of distilled acid was 8.1 g (81 %), n_D^{20} 1.4126. Normal caproic acid, n_D^{20} 1.4163.

Perdeuterio-n-Undecanone-6.

A mixture of 8.0 g of iron powder and 8.0 g of deuterated hexanoic acid prepared above was slowly heated to 270° in a bath of Woods metal until evolution of carbon dioxide and hydrogen ceased. The residue was extracted with ether, the solution was filtered and evaporated on the steam bath. The oil was distilled in a Späth bulb. Yield : 4.65 g (77 5.%), n_D^{20} 1.4226.

Mass analysis : $C_{11}D_{22}O$,   55.3 %
                 $C_{11}D_{21}HO$,   34.6 %
                 $C_{11}D_{20}H_2O$, 10.1 %

The ketone (2.3 g) was exchanged twice with 8 ml C_2H_5OD and 1.5 ml D_2O by heating the solution under reflux for 16 hours in the presence of a few mgm of potassium carbonate. The solvent was removed on the

vacuum line and the residue was purified by distillation in a Späth bulb. Yield : 1.95 grams.

Mass analysis : $C_{11}D_{22}O$,   75.83 %
                 $C_{11}D_{21}HO$,   14.93
                 $C_{11}D_{20}H_2O$,   3.34
Atom % D : 97.2.

6-Hydroxy-6-protio-n-deuterioundecane, $CD_3(CD_2)_4CH(OH)(CD_2)_4CD_3$.

The above ketone (2.4 g; 0.01 mol) was reduced to the alcohol with $LiAlH_4$ (1.37 g as described above in the preparation of the hexyl alcohols. Yield : 2.3 g (95 %), n_D^{20} 1.4312.

6-Bromo-6-protio-n-deuterioundecane, $CD_3(CD_2)_4CHBr(CD_2)_4CD_3$.

The alcohol (2.2 g; 0.01 mol) was converted into the bromide by heating it with a mixture of 48 % hydrobromic acid (4.36 g) and concentrated sulphuric acid (1.37 g) as described in the preparation of the deuterated hexyl bromides above. Yield : 2.5 g (86 %), n_D^{20} 1.4527.

6,6-Diprotio-n-deuterioundecane, $CD_3(CD_2)_4CH_2(CD_2)_4CD_3$ *(V)*.

The reductive debromination was carried out with 2.5 g (0.0085 mol) of the bromide, zinc dust (3.0 g) and acetic acid (20 ml). The product was isolated as described above for the dodecanes. Yield : 1.4 g (81 %), n_D^{20} 1.4128. For normal *n*-undecane, n^{20} is 1.4164.

Mass analysis : $C_{11}D_{22}H_2$, 66.4 mol %
                 $C_{11}D_{21}H_3$, 27.0
                 $C_{11}D_{20}H_4$,   5.5
                 $C_{11}D_{19}H_5$,   1.0
Atom % D : 97.1.

6-Keto-5,5,7,7-tetraprotiodeuterio-n-undecane,
$CD_3(CD_2)_3CH_2COCH_2(CD_2)_3CD_3$.

The completely deuterated ketone (4.45 g; 0.0235 mol) was exchanged eight times with methanol (50 ml) water (10 ml) and a trace of potassium carbonate. Each time the solution was heated under reflux for one day. The solvent was then distilled off and the residue taken up in ether and distilled from a Späth bulb. Three grams of ketone were recovered.

Mass analysis : $C_{11}D_{18}H_4$, 74.9 mol %
                 $C_{11}D_{19}H_3$,   6.27
                 $C_{11}D_{18}H_4$,   6.9

6-Hydroxy-5,5,6,7,7-pentaprotiodeuterio-n-undecane,
$CD_3(CD_2б_3CH_2CH(OH6CH_2(CD_2б_3CD_3$.

The above ketone (1.8 g) was reduced to the alcohol with $LiAlH_4$ in ether as already described. Yield : 1.7 g (93 %), n_D^{20} 1.4320.

6-Bromo-5,5,6,7,7-pentaprotiodeuterio-n-undecane,
$CD_3(CD_2)_3CH_2CHBrCH_2(CD_2)_3CD_3$.

The bromide was prepared from the alcohol as already described. From 1.7 g of alcohol there was obtained 1.65 g (73 %) of the bromide, n^{20} 1.4520.

5,5,6,6,7,7-Hexaprotioperdeuterio-n-undecane,
$CD_3(CD_2)_3(CH_2)_3(CD_2)_3CD_3$ *(VI)*.

The bromide was debrominated with zinc dust (2.0 g) in acetic acid (15 ml). Yield : 0.90 g (72 %), n_D^{20} 1.4130.

Mass analysis : $C_{11}D_{18}H_6$,   83.7 mol %
$C_{11}D_{17}H_7$,   14.5
$C_{11}D_{16}H_8$,   1.5

6-Hydroxy-5,5,7,7-tetraprotiodeuterio-n-undecane,
$CD_3(CD_2)_3CH_2CD(OH)CH_2(CD_2)_3CD_3$.

The ketone was reduced as already described with $LiAlD_4$ in ether. Yield : 2.1 g (90 %), $n_{i)}^{2?}$ 1.4318.

6-Bromo-5,5,7,7-tetraprotiodeuterio-n-undecane,
$CD_3(CD_2)_3CH_2CDBrCH_2(CD_2)_3CD_3$.

The alcohol prepared above was converted into the bromide with a mixture of 4.16 g 48 % hydrobromic acid and 1.3 g of concentrated sulphuric acid. Yield : 2.17 g (78 %), n_D^{20} 1.4516.

5,5,7,7-Tetraprotiodeuterio-n-undecane,
$CD_3(CD_2)_3CH_2CD_2CH_2(CD_2)_3CD_3$ *(VII)*.

The bromide was converted into the hydrocarbon with zinc dust (1.85 g) in deuterium oxide (0.5 ml) and anhydrous dioxane (10 ml). Yield : 1.1 g (73 %), n_D^{20} 1.4127. Beilstein test negative.

Mass analysis : $C_{11}D_{20}H_4$,   69.6 mol %
$C_{11}D_{19}H_5$,   18.1
$C_{11}D_{18}H_6$,   2.6

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