

**Organic Syntheses with Heavy
Isotopes**
**Attempted Synthesis of Perdeuterio-
Behenic Acid**

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With the intention to compare the phase transitions in monomolecular films of behenic acid¹ with those of its heavy isotopic analogue, a synthesis of perdeuterio-behenic acid has been attempted. It was performed with only classical chemical reactions. The main difficulty has been to avoid loss of deuterium in the various steps of the synthesis. It is quite evident that work of this type cannot be undertaken without mass spectrometric analysis of all intermediate products. The final product consists of a mixture of deuterio-behenic acids from $C_{22}H_{18}D_{26}O_2$ to $C_{22}H_1D_{13}O_2$, with $C_{22}H_7D_{37}O_2$ as the most abundant component. The end product together with the principal intermediate compounds and the mode of preparation are given in Chart 1.

Preparation of tetradeuterio-succinic acid (III) and some of its derivatives (II, IV) was executed according to the procedure of McLean and Adams². Dideuterio-malonic acid- d_2 (XII) and trideuterio-acetic acid- d (XIII) were prepared according to the technique reported by Halford and Anderson³.

Catalytic hydrogenation of dimethyl acetylene dicarboxylate (I) with pure deuterium using deuterium-reduced Adams' catalyst in dry ethyl acetate gave dimethyl deuterio-succinate (II). This was converted into deuterio-succinic acid (III) by hydrolysis with water containing a small amount of nitric acid. The acid was transformed to deuterio-succinic anhydride (IV) by means of acetic anhydride. Methyl hydrogen deuterio-succinate (V) was obtained by refluxing the anhydride with absolute methanol.

Kolbe's anodic condensation⁴ has been a valuable method for the preparation of dimethyl deuterio-adipate (VI), dimethyl deuterio-sebacate (VIII), dimethyl deuterio-octadecane-1,18-dioate (X), methyl deuterio-caproate

(XIV) and methyl deuterio-behenate (XVI). In electrolyses the monocarboxylic acids (XIII, XV) and/or half-esters of dicarboxylic acids (V, VII, IX, etc.) were previously totally neutralized with sodium methoxide, and the reaction conducted in methanolic solutions. For preparation of dimethyl deuterio-adipate (VI), the reaction may be carried out⁵ with equivalent amounts of deuterio-succinic anhydride (IV) and sodium in methanol. The electrolyses were performed by using a cell previously described by the author⁶, where mercury is employed as the cathode and a rotating platinum sheet as the anode. During the reaction the temperature was not allowed to exceed 50°.

In the alkaline hydrolysis, the temperature was rigorously controlled. It was observed that when dimethyl deuterio-adipate (VI) was submitted to a partial hydrolysis with $NaOCH_3$ at 80°, a half-ester was obtained which had a density lower than that of a specimen obtained from hydrolysis with KOH at 40°. Infrared and mass spectrometric analyses showed that these half-esters differed in deuterium content. In the hydrolysis at 80° a partial replacement of deuterium by hydrogen evidently took place.

The melting points, densities and refractive indices of the deuterium-containing compounds were determined and compared with those of their light hydrogen analogues. With the exception of the anhydride, it was noted that under the same conditions the deuterium-containing compounds

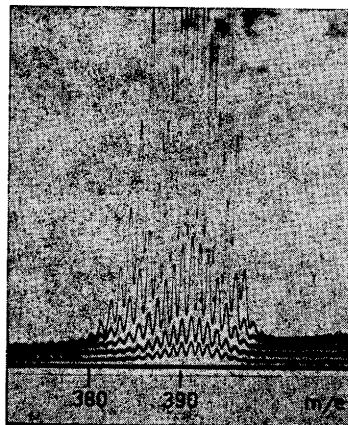
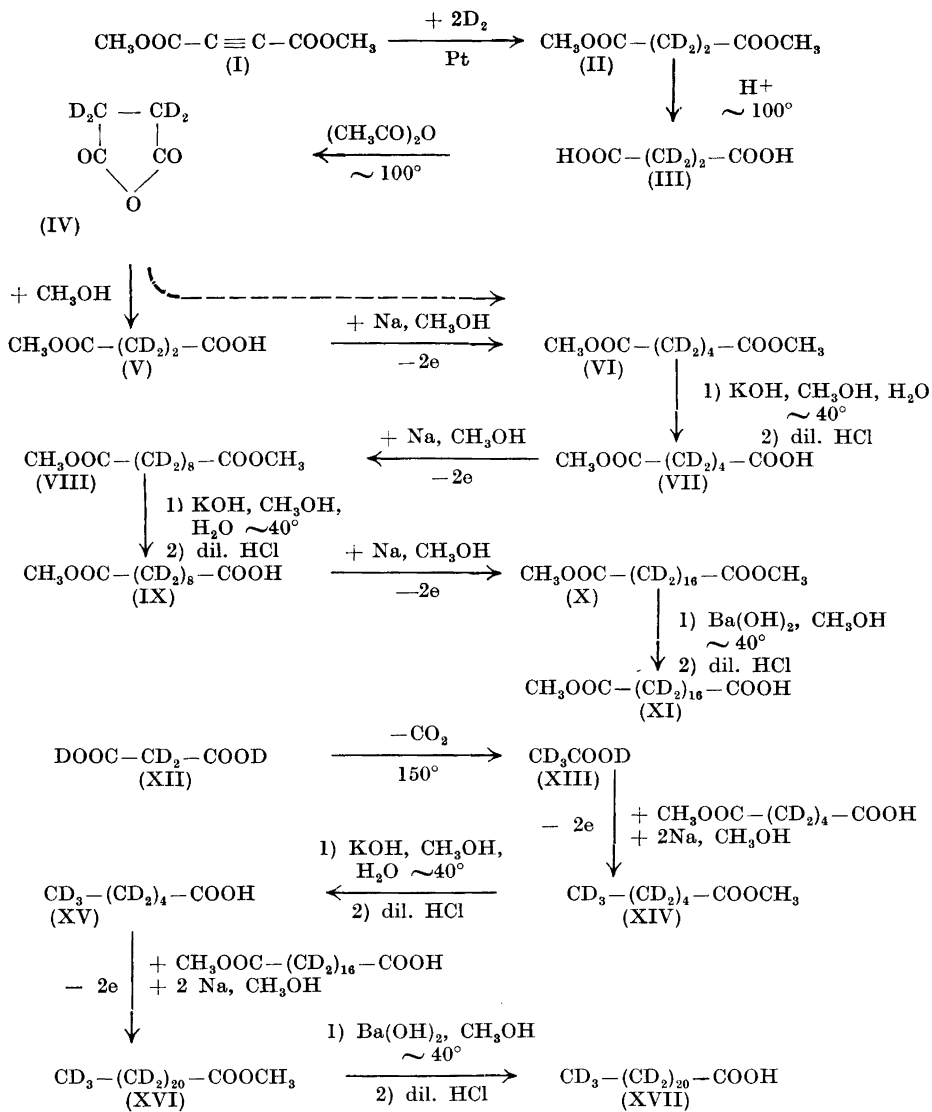


Fig. 1. The high-mass end of mass spectrum of methyl deuterio-behenate.

Chart 1.



generally have lower melting points^{2,3,7} and lower refractive indices than the light hydrogen analogues, but the latter have lower densities².

Infrared spectrometric analyses of these deuterium compounds have been performed and the results will be the subject of a separate communication.

With the exception of the dideuterio-malic acid- d_2 (XII), all deuterium compounds were submitted to mass spectrometric analysis. Spectra of these products were compared with those of the light hydrogen analogues, which have been published by Ryhage and Stenhagen⁸, and from that comparison the deuterium content of each product has been qualitatively determined. The high-mass end of the mass spectrum of the methyl deuterio-behenate reproduced in Fig. 1 shows a series of molecule-ion peaks from m/e 380 to m/e 397, corresponding to a series of esters of varying deuterium content from $C_{23}H_{20}D_{26}O_2$ to $C_{23}H_3D_{43}O_2$. The prominent peak at m/e 391 corresponds to the highest concentration of methyl heptatriadeuterio-behenate ($C_{23}H_9D_{37}O_2$) in the synthesized product. It is evident from Fig. 1 that molecules of mass 397, corresponding to the methyl perdeuterio-behenate (XVI), have been present, because the peak at m/e 397 is higher than that expected for the ^{13}C isotope peak of m/e 396.

Full details will be published later.

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Isolation of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone from Lignin

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According to the work of Hibbert¹, a series of guaiacylpropanones (III a-d) is formed from softwood lignin on heating with ethanolic hydrochloric acid for 48 h ("ethanolysis"). It was suggested¹ that these products originated from a structure of type II (3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone) or its enol form ("β-oxyconiferyl alcohol") assumed to be part of the lignin molecule. Later, it was proposed^{2,3} that the ketones III originate from arylglycerol-β-aryl ether structures (I), the ketol II being an intermediate in the ethanolysis process rather than a genuine structural element of lignin. This view was supported by the finding that ethanolysis of model compounds of type I yielded "Hibbert ketones" (III a, c, d); similarly, ketones III c, d and e were obtained on "acidolysis" (heating with 0.2 N HCl in dioxane-water (9:1)) of lignin as well as of the model compounds of type I³.

In order to obtain further evidence for the presence of structure I in lignin and of

