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Synthesis of Deuterium-labelled Polyoctylalkanes

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ABSTRACT

The synthesis of specifically labelled 9-*d*-9-octylheptadecane (**1**) and 9-*d*-9,10-dioctyloctadecane (**2**) has been achieved using selective and specific deuterium labelling methods. The precursor to the latter compound, tetraoctyl ethene, has been achieved by a variant of the McMurry reaction which improves upon recently published methods.

Keywords: Triethylsilyl deuteride, McMurry reaction

INTRODUCTION

In our work on the application of NMR spectroscopy to the analysis of molecular motion in alkanes used as lubricants and energy-transfer fluids[1] we have made studies of synthetic analogues of the poly-α-olefins which are an essential feedstock in the industry. In order to identify specific effects associated with particular carbon atoms the synthesis of a number of deuteriated poly-octyl alkanes was undertaken. Deuterium is particularly useful since the rate of overall motion can be determined directly from deuterium-NMR spectroscopy. Although the hydrocarbons themselves were often amenable to predictible synthetic routes, the incorporation of heavy hydrogen at specific defined carbon atoms, an essential of the analytical method, was much less readily achieved.

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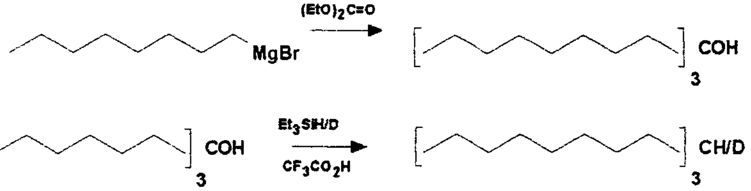
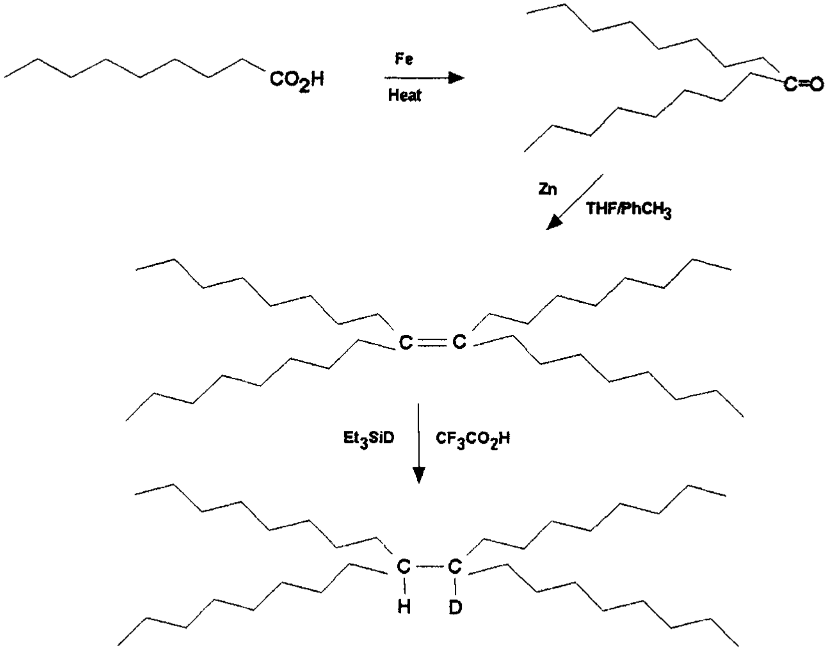
DISCUSSION

The present work deals with the synthesis of 1 and 2 by unambiguous methods. Although the hydrocarbon may be made by a number of methods in principle, some of these (*e.g.* reduction of the tertiary alkyl chloride by $LiAlH_4$) failed because the basic reaction conditions also promoted dehydrohalogenation, Hydrogenolysis is also inherently applicable, but suffers from the rearrangement of the side-chains which Lewis acids promote.



Scheme 1: Synthesis of 9-*d*-9-octylheptadecane

We therefore sought to use "ionic hydrogenation" in which a tertiary carbonium ion, formed from the tertiary alcohol with CF_3CO_2H, was reacted with incipient hydride (deuteride) anion from $Et_3SiH(D)$. In the synthesis of 2, gas liquid chromatography showed the formation of the isomeric 9-10-dioctyloctadeca-8-enes, but since the



Scheme 2: Synthesis of 9-*d*-9,10-dioctyloctadecane

equilibrium with the derived carbonium ions substantially favours the tertiary cation all three of the isomeric alkenes in equilibrium with this ion were consumed to formed the same alkane.

The synthesis of 9,10-dioctyloctadec-9-ene by the McMurry reaction was brought about cheaply and efficiently by using a mixture of hydrocarbon (toluene) and ether (THF or dioxan) solvents. Neither alone was successful; unreacted ketone was present even after many hours and the process was inefficient and slow.

The synthesis of 9-heptadecanone from nonanoic acid was readily achieved using iron; this process took place readily at atmospheric pressure and did not require distilling the acid over catalysts (e.g. MnO) heated in furnaces, as in earlier processes.

^{13}C-NMR spectrscopy was particularly useful in confirming the presence of deuterium and the absence of the light hydrogen isotopic impurity. Figure 1 shows the spectrum of

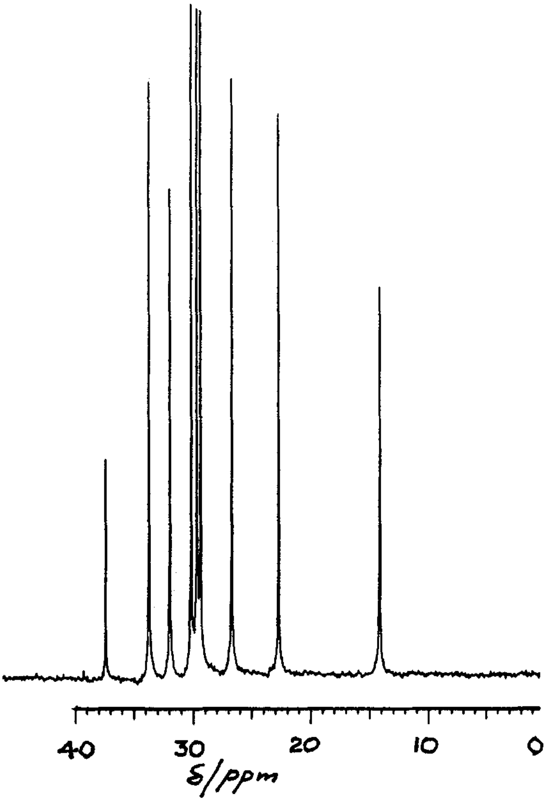


Figure 1: ^{13}C-NMR Spectrum of 9-octylheptadecane

9-*h*-9-octylheptadecane; the tertiary carbon atom shows as a singlet at δ, 37.43. Figure 2 shows the corresponding spectrum of 9-*d*-9-octylheptadecane. Here the tertiary carbon atom shows a triplet centred at δ, 36.85, owing to C-D coupling. No evidence of the C-H system can be found. Similarly, Figure 3 shows the spectrum of 9,10-dioctyloctadecane, where the two tertiary carbon atoms appear at δ, 39.496. The mono-deuteriated analogue, shown in Figure 4, demonstrates the presence of both C-H (singlet; δ, 37.46) and C-D (triplet; δ, 36.87). The adjacent CH_2 systems at δ, 33.68 are incompletely resolved but quite clearly evident. (The chosen detail of the spectrum omits the methyl absorbance at δ, 14.141 ppm.)

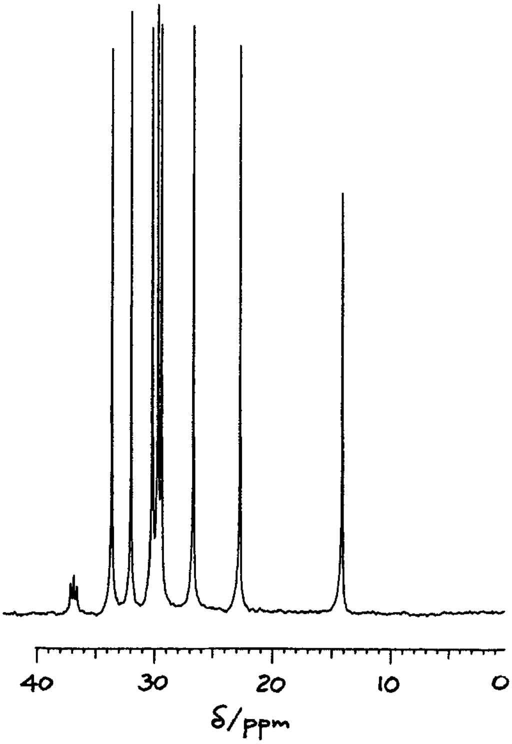


Figure 2: ^{13}C-NMR Spectrum of 9-*d*-9-octylheptadecane

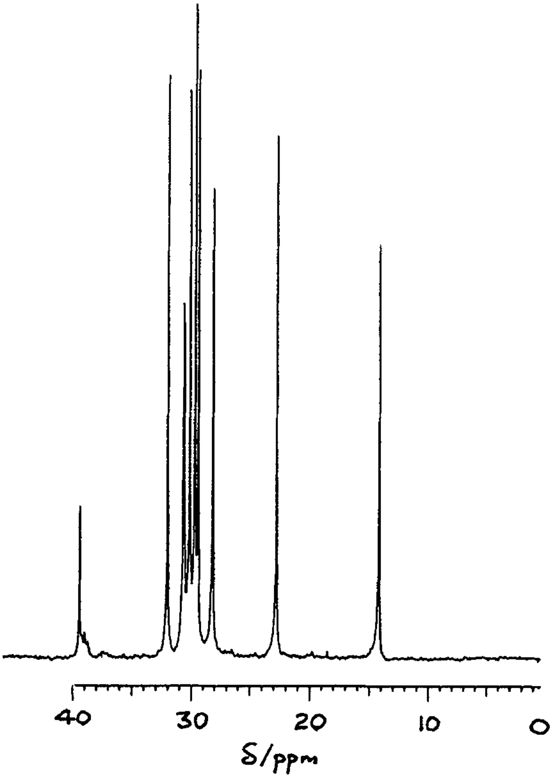


Figure 3: ^{13}C-NMR Spectrum of 9,10-dioctyloctadecane

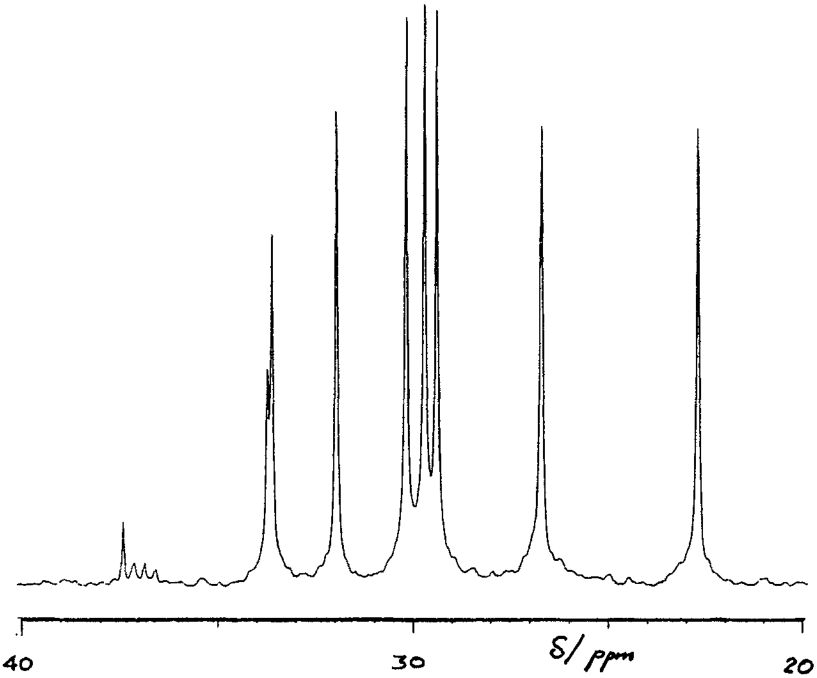


Figure 4: Detail of ^{13}C-NMR Spectrum of 9-*d*-9,10-dioctyloctadecane (20-40 ppm region)

EXPERIMENTAL

Gas-liquid chromatography was carried out using a DB5 (substituted siloxane copolymer film) capillary column in a Carlo Erba FTV 2150 programmable machine. Hydrogen was used as carrier gas, with FID detection. NMR measurements were in $CDCl_3$ solution, using TMS standard, on a Bruker AC300 instrument, at 67.83 MHz (^{13}C).

9-Heptadecanone (di-n-octyl ketone) from nonanoic acid (100 g., 0.63 mol) by heating this under nitrogen with hydrogen-reduced iron powder (17 h., 0.32 mol).[2] At 130° hydrogen began to be evolved, and the temperature was held below 180° until this had ceased (1.5 h.). Cautious heating to 260° caused the evolution of carbon dioxide over 1 hour, after which the crude ketone was isolated by distillation at atmospheric pressure. This material was recrystallised from aqueous ethanol (400 ml.) to give 65-75 g. (80-90%) of 9-heptadecanone, m.p. 50.5-51.5° (lit.48-48.5°, 52-3°, 53;°[3] . >99% by g.l.c. and ^{1}H-NMR)). The decarboxylation step should not be extended past one hour, when the yield of ketone falls sharply and its isolation becomes much more difficult.

9-Octylheptadecan-9-ol

9-Octylheptadecane (tri-n-octylmethane, 1) has been prepared[4] by the dehydration of 9-octylheptadecan-9-ol and hydrogenation of the resulting olefinic species. Using the general method of Moyer and Marvel,[5] we obtained 9-octylheptadecan-9-ol (tri-n-octyl carbinol) in 70-80% yields from the reaction of diethyl carbonate (18.5 g., 0.167 mol) with octylmagnesium bromide from magnesium (13.5 g., 0.55 mol) and octyl bromide (106 g., 0.55 mol) in anhydrous ether (125 ml), followed by boiling under reflux for 1 h... After hydrolysis (NH_4Cl-ice) and removal of solvent from the ether extract, crude 9-octylheptadecan-9-ol (65 g., 70-80% by g.l.c.; 70-80% overall) was obtained as a viscous oil (^{1}H-NMR δ: 0.93 (t, J 6 Hz, 9H, CH_3), 1.28 (bs, ca. 36H, CH_2), 1.39 (bs, 7H, CH_2 and OH). ^{13}C-NMR: δ: 14.09 (CH_3), 22.67, 23.49, 29.30, 29.50, 30.20, 31.69, 39.20 (CH_2), 74.45 (C(OH)). This material could be dehydrated by heating it (65 g.) with a few crystals of iodine[6] in a fractional distillation apparatus under total reflux at 0.2 mmHg. *9-octylheptadec-8-ene* (36.5 g., 60% yield. ^{1}H-NMR δ: 0.89 (t, J 8 Hz, 3 x CH_3), 1.37 (bs, 34H, 17 x CH_2), 1.94 (bq, J 6 and 8 Hz, 6H, 3 x CH_2-C=C), 5.08 (t, J 6 Hz, 1H, CH_2-CH=C) was then distilled from the mixture (b.p. 167-170° /0.07 mmHg). 9-Octylheptadecane (^{13}C-NMR δ: 14.11 (3 x CH_3), 22.69, 26.78, 29.40, 29.69, 30.17, 31.94, 33.70, (7 x 3 x CH_2), 37.40 (CH)) was then obtained (36.7 g.) in quantitative yield upon hydrogenation. (cyclohexane (50 ml.) - glacial acetic acid (50 ml.), 200 psi, 80°, 24 h., with . 5% Pd/C (2 g)).

The dehydration of 9-octylheptadecan-9-ol (56 g.,) by heating with dimethyl sulfoxide[7] gave a malodorous yellow product (34.6 g., b.p. 180-188°/0.2 mmHg) which was partially purified by passage in pentane through silica gel to give a colourless oil (32.5 g.) which yielded the alkane (24.7 g., b.p. 180-181°/0.19 mmHg). This alkene (12 g.) was dissolved in cyclohexane (15 ml.) and was allowed to stand for 24 h. over Raney nickel to remove all traces of residual sulfur. Upon hydrogenation (200 psi, 80°, 12 h., using 5% Pd/C (1 g.)) crude 1 (9.9 g., b.p. 182°/0.1 mmHg) was obtained.

This material was impure, appearing to contain an aromatic impurity (^{13}C-NMR). Further purification was achieved by shaking the cyclohexane solution of this material with cold concentrated sulfuric acid, which removed alkenic and aromatic species and gave a product (6.0 g.) which, although it was substantially pure by ^{13}C-NMR spectroscopy, was 85% pure by g.l.c..

The synthesis of the deuterium isotopomer, 1, was more difficult. Although a range of textbook processes are applicable, dehydration and deuterium scrambling made such methods useless. Thus, the reduction of the corresponding chloride or bromide by $LiAlD_4$ gave a mixture of alkane and alkene, as shown by gas-liquid chromatography.

9,10-dioctyloctadec-9-ene

Similarly, the synthesis of 9,10-dioctyloctadecene from 9-heptadecanone (di octyl ketone) could generally be achieved with difficulty and in low yields when the common variants of the McMurry reaction were used. However, the use of a mixture of toluene and tetrahydrofuran allowed $TiCl_4$ to be reduced by zinc to a dark-red suspension of low-valent titanium species. In contast with the recently reported experience of Fürstner and Seidel,[8] who advocated the use of high-surface sodium as a reducing agent of the more expensive Ti(III) but who found this to give a mixture of reduction products with aliphatic carbonyl compounds, the use of THF-toluene mixtures allowed the synthesis of 4 in good yield (70%) and high purity (>99%).

Dry zinc grit (25 g., 0.38 mol), dry tetrahydrofuran (100 ml.) and dry toluene (150 ml.) were stirred vigorously under a nitrogen atmosphere for 15 minutes to remove traces of oxygen in the solvent. Then, under reflux, titanium(IV) chloride (37.5 g., 22.0 ml., 0.20 mol) was added dropwise with ice-cooling to the vigorously-stirred solution. A yellow solution resulted, and the flask filled with yellow fumes and deposits. On removing the ice bath and heating the mxiture to reflux for 30-40 minutes the fumes and deposits were resorbed into the solution, which passed from yellow to green and finally formed a dense, dark-red solution.

This was allowed to cool slightly and the rate of stirring was diminished. A solution of 9-heptadecanone (25.4 g., 0.10 mol) in dry toluene (220 ml.) was added quite rapidly. When the initial mildly exothermic reaction has abated, the mixture was boiled under reflux for 90 minutes. On cooling and treatment with an excess of dilute sulphuric acid gave an easily separated organic phase containing the required alkene, which was isomerically pure (g.l.c.), in 70% yield. Quenching the reaction by adding an excess of base gave voluminous precipitates of titanium species whose separation and extraction led to considerable mechanical losses.

In a similar reaction in anhydrous dioxan (300 ml.) zinc grit (30 g., 0.46 mol) was reacted with titanium(IV) chloride (30 g., 0.154 mol) to give the low-valent titanium species. The subsequent addition of 9-heptadecanone (26 g., 0.102 mol) and six hours' boiling gave, after hydrolysis (saturated aq. K_2CO_3) and hexane extraction, 9,10-dioctyloctadec-9-ene (75% based upon ketone consumed).

9-d-9-Octylheptadecane

The reduction of triethylchlorosilane (50 g.) by the stoichiometric quantity of lithium aluminium deuteride in boiling ether gave triethylsilane-d_1 (24 g., % b.p. 107-109°. Si-D absorption, 1550 cm^{-1}; no Si-H observed at 2100 cm^{-1} (i.r.)).[9]

A solution of 9,10-dioctyloctadec-9-ene, excess of trifluoroacetic acid, and an equimolar amount of triethylsilane-d_1 in dichloromethane was stirred for seven days.[10] The progress of the reaction was follwed by g.l.c., which showed the presence of the isomeric *E*- and *Z*-9-octyloctadec-8-enes (*E*/*Z*, 2:1) in dynamic equilibrium with the parent alkene. Short-path high-vacuum distillation of the resulting oil, followed by passage of the pentane solution over silica gel, gave a pure sample of 9-D-9,10-dioctyl-octadecane (4 g.) as dedfined by ^{1}H- and ^{13}C-NMR spectroscopy.

9-d-9-octylheptadecane

In the same way and under the same reaction conditions, 9-octylheptadec-8-ene (from 9-octylheptadecan-9-ol) underwent reaction weith trifluoroacetic acid and triethylsilane-d_1 in dichloromethane to give 9-*d*-9-octylheptadecane, which was purified by the same combination of short-path distillation and column chromatography.

Acknowledgements

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