## A Direct Preparation of Fully Deuterated High-molecular-weight Hydrocarbons

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THERE is growing interest in methods of synthesizing isotopically labelled compounds in view of their widespread use in the study of reaction mechanisms both of a chemical and biological nature.

We report a general exchange procedure for the preparation of saturated fully deuterated hydrocarbons containing from 10 to 36 carbon atoms which complements several other recent syntheses of deuterated hydrocarbons.<sup>1-4</sup> Thus, Garnett and his co-workers have reported the use of DCl to label olefins<sup>1</sup> and Larson, Hightower, and Hall<sup>2</sup> have prepared a number of low-molecular-weight perdeuterated olefins using  $D_2$  gas and an alumina catalyst. Workers from this laboratory have also reported the use of the Wittig reaction to synthesize a number of specifically labelled olefins,<sup>3</sup> and Dixon and Marr<sup>4</sup> have reported the gas-phase exchange of octanes with  $D_2$  gas.

The latter technique, which has been used in several laboratories, is not applicable to the higher-molecular-weight nonvolatile hydrocarbons, and we have accordingly investigated and successfully developed a liquid-phase exchange procedure. The method consists of bubbling  $D_2$  gas through an exchange cell containing the hydrocarbon and a fixed bed of catalyst. Catalysts successfully investigated to date are Pd, Pt, and Rh (each 2%)

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on charcoal), and Raney nickel. During exchange the cell is immersed in an oil bath at  $150-200^{\circ}$ , depending on the volatility of the hydrocarbons. At the end of the exchange, the material is separated from the catalyst and either distilled or recrystallized. The compounds prepared by this technique are shown in the Table. This represents the first reported preparation of these materials in their deuterated form.

Since very little work has been done on the mechanism of liquid-phase exchanges, in contrast to the extensive investigations on gas-phase exchanges,<sup>5</sup> work has been started to elucidate the mechanistic aspects of this exchange.

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## TABLE

Starting material	Product	Analysis <sup>b</sup>	Temperature	Hr. of <sup>c</sup> exchange
n-Decane	<sup>2</sup> H <sub>22</sub> ]-n-Decane	96% D (i.r.)	$170^{\circ}$	282
n-Dodecane	[ <sup>2</sup> H <sub>26</sub> ]-n-Dodecane	98.6% D (mass)	195°	430
n-Hexadecane	[ <sup>2</sup> H <sub>34</sub> ]-n-Hexadecane	99.4% D (mass)	190°	316
n-Octadecane	[ <sup>2</sup> H <sub>38</sub> ]-n-Octadecane	97.9% D (n.m.r.)	$195^{\circ}$	1360
n-Tetracosane	[ <sup>2</sup> H <sub>50</sub> ]-n-Tetracosane	98.6° D (n.m.r.)	$195^{\circ}$	596
n-Octacosane	<sup>[2</sup> H <sub>58</sub> ]-n-Octacosane	97.9% D (mass	$195^{\circ}$	1500
n-Hexatriacontane	[ <sup>2</sup> H <sub>74</sub> ]-n-Hexatriacontane	99•5% D (mass)	$195^{\circ}$	1500
Pristane (2,6,10,14-Tetra-		, - , , ,		
methylpentadecane)	<sup>[2</sup> H <sub>40</sub> ]-Pristane	$99.6^{\circ}_{0}$ D (mass)	$195^\circ$	400
Squalane (2,6,10,15,19,23-		,,		
Hexamethyltetracosane)	[ <sup>2</sup> H <sub>62</sub> ]Squalane	99.5%D (mass)	$195^{\circ}$	1465
cis-Decalin	[ <sup>2</sup> H <sub>18</sub> ]Decalin <sup>d</sup>	99% D (n.m.r.)	$165^{\circ}$	496
trans-Decalin	[ <sup>2</sup> H <sub>18</sub> ]Decalin <sup>d</sup>	99% D (i.r.)	$175^{\circ}$	500
1,5,9-Cyclododecatriene	<sup>2</sup> H <sub>24</sub> ]Cyclododecane	99.5% D (mass)	195°	1210
Cyclododecane	[ <sup>2</sup> H <sub>24</sub> ]Cyclododecane	99% D (i.r.)	$195^{\circ}$	452
trans-Stilbene	[ <sup>2</sup> H <sub>26</sub> ]-1,2-Dicyclohexylethane	98.1% D (mass)	$185^{\circ}$	4720

Perdeuterated hydrocarbons prepared by exchange with dcuterium gasa

<sup>a</sup> The hydrocarbon-to-catalyst weight ratio was kept constant in all runs and the same catalyst  $(2^{\circ}_{10} \text{ Pd/C},$ 10-30 mesh) used throughout.

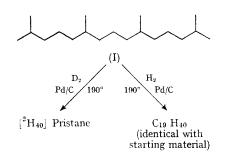
<sup>b</sup> Expressed as atom % deuterium with the analytical method in brackets.

<sup>e</sup> The hours of exchange have been adjusted to indicate the exchange rate relative to the 20 g. of n-hexadecane 3 equiv. of hydrogen).

<sup>4</sup> The  $[{}^{1}H_{18}]$  decalin obtained was 93% trans and 7% cis.

Cracking or skeletal isomerization is completely absent as evidenced by the chemical purity of the deuterated products obtained. This was firmly established in an experiment with pristane (I) in which the compound was subjected to H<sub>2</sub> passage under the exchange conditions for 700 hours. The recovered pristane had a mass-spectral cracking pattern identical with that of the starting material.

Epimerization at tertiary carbon atoms does occur as shown in the Table for the results with cis- and trans-decalin.  $[^{2}H_{40}]$ Pristane and  $[^{2}H_{62}]$ squalane undoubtedly are also obtained as a mixture of their stereoisomers.



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