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SOME NOVEL PERFLUOROALKANEDIOIC ACID DERIVATIVES AND α,ω-DI-IODOPERFLUOROALKANES

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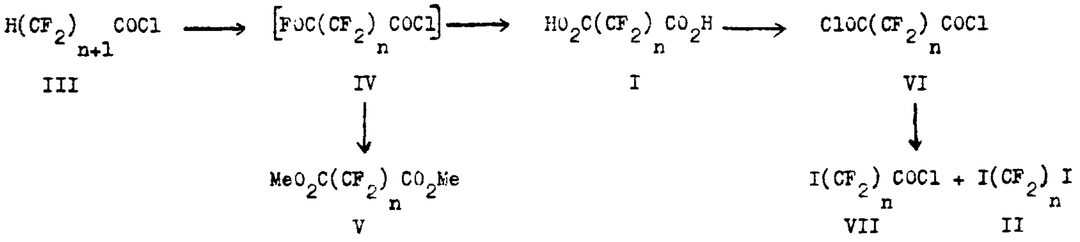
Perfluoroalkanedioic acids, $HO_2C(CF_2)_nCO_2H$ (I), and α,ω-di-iodoperfluoroalkanes, $I(CF_2)_nI$ (II), where n = 1,3,5,7, etc. were hitherto unknown for values of $n > 5$. In contrast, the corresponding compounds where n = 2,4,6,8, etc. are available by several routes (1,2,3,4). It has now been found possible to derive the compounds where n is odd from the acid chlorides III, which are readily available (5).

Fluorocarbons containing terminal difluoromethyl groups can be oxidised to fluorocarboxylic acids by reaction with mixtures of nitrogen dioxide and chlorine in the gas phase (6). This technique has now been applied to the acid chlorides III when n+1 = 4,8, and 10,



$$\begin{tikzcd}
H(CF_2)_{n+1}COCl \arrow[r] & \left[FOC(CF_2)_nCOCl\right] \arrow[r] \arrow[d] & HO_2C(CF_2)_nCO_2H \arrow[r] & ClOC(CF_2)_nCOCl \arrow[d] \\
\text{III} & MeO_2C(CF_2)_nCO_2Me & \text{I} & I(CF_2)_nCOCl + I(CF_2)_nI
\end{tikzcd}$$

III IV I VI

V VII II

and the crude oxidation products (IV) were converted into either dimethyl perfluoroalkanedioates (V) or perfluoroalkanedioic acids (I); the acids were then converted into perfluoroalkanedioyl dichlorides (VI). The overall yields of V or VI were generally between 30 and 50%, the major by-products being derivatives of the perfluoroalkanedioic acids $HO_2C(CF_2)_{n-1}CO_2H$, obtained in 10 to 15% yields. Some physical constants of the esters V (characterised by elemental analysis and mass spectroscopy) are shown in the Table.

Fluoroalkanoyl chlorides react with potassium iodide at 200° in a sealed vessel to give fluoroalkyl iodides (7). It has now been found that the passage of fluoroalkanoyl chlorides through a glass tube packed with crystalline potasium iodide (dried at 200°) at temperatures between 270 and 375°, gives fluoroalkyl iodides and carbon monoxide. When a perfluoroalkanedioyl dichloride of the type VI is treated in this manner, the product consists of an α,ω-di-iodoperfluoroalkane (II), an ω-iodoperfluoroalkanoyl chloride (VII), and, at the lower temperatures of operation, the starting material (VI). The ratio of the products can be controlled by the rate of addition of the acid chloride (VI), the temperature of the tube, and by recycling the mixture. On several occasions, VI, n = 3 (*ca* 500g) was so treated giving II, n = 3 (50 - 60%) and VII, n = 3 (5 - 20%), the latter isolated as the free acid. On a smaller scale, VI, n = 7 containing VI, n = 6, and VI, n = 9 containing VI, n = 8 were converted into the corresponding mixtures of di-iodides II. Some physical constants of these products (characterised by elemental analysis) are given in the Table below.

Compound	Boiling point	Melting point	Refractive index, n_D^{20}
$MeO_2C(CF_2)_6CO_2Me$	236° a		1.3415
$MeO_2C(CF_2)_7CO_2Me$	249°		1.3400
$MeO_2C(CF_2)_8CO_2Me$	261° b		1.3394
$MeO_2C(CF_2)_9CO_2Me$	275°	31-2°	1.3314 c
$I(CF_2)_3CO_2H$	107-8°/35 mm Hg	31-4°	
$I(CF_2)_6I$		25°	
$I(CF_2)_7I$		51-2°	
$I(CF_2)_8I$		75-6°	
$I(CF_2)_9I$		94-5	

a 126-7°/25 mm Hg (2)   b 144-6°/25 mm Hg (2)   c at 36°

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