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FLUORINATIONS WITH POTASSIUM TETRAFLUOROCOBALTATE(III). PART IV*. FLUORINATION OF NAPHTHALENE

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Summary

Fluorination of naphthalene with potassium tetrafluorocobaltate(III) yielded three major products identified as hexadecafluorobicyclo[4,4,0]-deca-1(6)-ene, 3*H*-pentadecafluorobicyclo[4,4,0]deca-1(6)-ene and tetradecafluorobicyclo[4,4,0]deca-1(6),3(4)-diene. Dehydrofluorination of the 3*H* compound afforded the above diene and its isomer tetradecafluorobicyclo[4,4,0]deca-1(6),2(3)-diene. The mechanism of the fluorination is discussed in terms of oxidation.

Introduction

Tetralin has been fluorinated exhaustively over cobaltic fluoride in order to optimise the production of fluorocarbon and a good yield of perfluorodecalin has been obtained [2]. Subsequently [3], this compound was separated into *cis* and *trans* isomers. Recently [4] the fluorinations have been repeated under milder conditions to give a complex mixture of polyfluorides, apparently largely polyfluorodecalins with a few hydrogen substituents. The four mono-hydro isomers derivable directly from tetralin (*cis*- and *trans*-2*H*- and 3*H*-heptadecafluorodecalins) were isolated and characterised.

Results and discussion

We now report the fluorinations of naphthalene and tetralin over potassium tetrafluorocobaltate(III) [5]. This reagent is milder than cobalt(III) fluoride for the fluorinations of benzene and some aliphatic compounds, but it now appears that with aromatic polycycles the major products are unsaturated fluorocarbons. From naphthalene a relatively simple product

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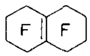
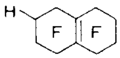
[*] For Part III, see ref. 1.

mixture was obtained containing three major and a number of minor higher boiling compounds. Separation of the mixture by a combination of fractional distillation and gas chromatography afforded the three major components pure. The first was shown by its IR spectrum to be hexadecafluorobicyclo[4,4,0]deca-1(6)-ene (I) (58%), identical to the product obtained from the fluorination of octafluoronaphthalene with cobaltic fluoride [6]. The second and least abundant of the three isolated compounds (8.3%) was shown by IR spectroscopy and mass spectrometry to be a tetradecafluorobicyclo-decadiene. ^{19}F NMR spectroscopy indicated a symmetrical structure and suggested two identical pairs of fluorine atoms between double bonds, and four other pairs of fluorine atoms arranged in two identical pairs. The UV spectrum of the product suggested that the double bonds were not conjugated. Thus the product appeared to be tetradecafluorobicyclo[4,4,0]deca-1(6),3(4)-diene(II).

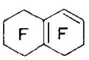


(I)

(II)



(III)



(IV)

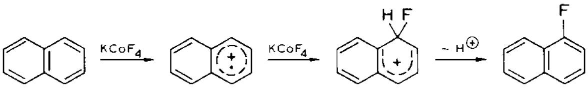
Confirmation came directly from a determination of the structure of the third component (III) (33.3%). Mass spectrometry and elemental analysis indicated this to be a pentadecafluorobicyclo-decene although the IR spectrum showed no double-bond absorption. ^{19}F NMR spectroscopy suggested the presence of a CHF group, non-equivalent CF_2 groups α to a double bond and three other CF_2 groups. There remained the problem of the position of the CHF group which could be either α or β to the double bond. Assuming no rearrangement of double bonds were to occur, dehydrofluorination of a compound with an α-CHF group should only give a conjugated diene, whereas one with a β-CHF group should give two dienes, one conjugated. On dehydrofluorination, the component in fact gave two dienes, one of which was identical to the second component of the fluorination mixture (II) and the other was its isomer (IV) which showed UV absorption. These data therefore indicate the product to be 3*H*-pentadecafluorobicyclo[4,4,0]deca-1(6)-ene (III).

Fluorination of tetralin in the same way gives a similar mixture of products but in lower yield. Presumably this arises by development of unsaturation in the tetralin by fluorination–dehydrofluorination, which may go as far as the fully aromatic structure. The lower yield obtained may reflect the difficulty of this process.

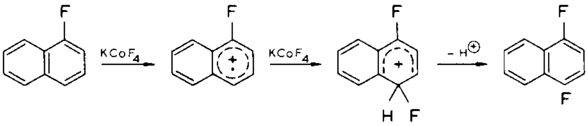
The relative simplicity of the mixture obtained from this fluorination is at first sight surprising when compared to the complex mixtures obtained from the fluorination of benzene with both cobalt trifluoride [7] and potassium tetrafluorocobaltate(III) [5]. These mixtures consist of many hydrogen-containing products, saturated in the former case and unsaturated in the latter.

Recently, a possible mechanism of fluorination based on oxidation of the organic substrate has been proposed [8] ; further, the electrochemical fluorination of naphthalene has been described [9] yielding as principal products 1-fluoro- and 1,4-difluoro-naphthalene, 1,1,4,4-tetrafluoro-1,4-dihydronaphthalene and a little 1,2,3,4-tetrafluoronaphthalene. Application of the oxidation principle to the latter fluorination is in accord with the observed results.

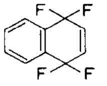
If the oxidation theory is applied to the fluorination of naphthalene, the following sequence could occur:



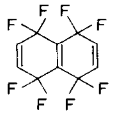
In the first step $KCoF_4$ acts as an oxidising agent and in the second step as a source of fluorine atoms. There is now a choice as to which ring is oxidised and it appears from electrochemical studies [9] that 1-fluoronaphthalene is oxidised in the fluorinated ring at a lower potential than naphthalene (1.6 V *vs.* 1.8 V). (Note also that fluorobenzene has a lower oxidation potential than C_6H_6.) Thus, the above sequence could be followed by that below.



By analogy with earlier examples [8], 1,4-addition could then follow to give (V). The isolated double bond of this should now be more difficult to oxidise than an aromatic ring and so successive repetition in the second ring would yield (VI) which can now be fluorinated to alicyclic products.



(V)



(VI)

A major objection to this is the lack of hydrogen-containing products as major components in the mixture. It may well be therefore that an alternative pathway applies and that 1,4-difluoronaphthalene is further fluorinated, as in the electrochemical process, by extensions of the "aromatic substitution" pathways typified by the above equations, leading eventually to octafluoronaphthalene. Recent evidence on the isolation of perfluoroaromatic products when caesium tetrafluorocobaltate(III) is used as a fluorinating agent suggests that this may be true [10]. Octafluoronaphthalene could then be saturated to give the observed major products.

It seems likely that both pathways operate in all cases but that the aromatic substitution route predominates when alkali metal cobaltates, particularly that of caesium, are used with polycyclic aromatics so that largely fluorocarbon products are formed. With cobalt(III)fluoride itself, however, the 1,4-addition route is favoured. Potassium tetrafluorocobaltate(III) gives unsaturated fluorocarbon products with anthracene and phenanthrene [11]

Experimental

Apparatus

Fluorinations were carried out in conventional reactors as previously described containing 2 - 10 kg of potassium tetrafluorocobaltate(III) at *ca.* 300 °C. The products were fractionally distilled, first through a 1.3 m vacuum-jacketed glass column packed with Dixon gauze rings and then through a 60.9 cm annular spinning-band column using a Teflon band.

Fluorination

In a typical run, naphthalene (50 g) was added as a melt to the reactor (containing 6 kg of $KCoF_4$) at 300 °C over a period of 70 min in a stream of nitrogen at 25 l h^{-1}. The product (124 g), which was collected in traps cooled in Dricold, was washed with water and sodium bicarbonate and again with water. The combined products from several runs (457 g) were fractionated first through the packed column to give a combined fraction (281 g), boiling range 109 - 170 °C, shown to be mainly three components. Further distillation of the fraction was then carried out using the spinning-band column employing a reflux ratio of 60:1 to give a fraction (78 g) in the boiling range 109 - 150 °C.

Fluorination of tetralin (60 g) in the same way as above gave an identical mixture of products (62 g).

Separation

An aliquot (2 g) of the fraction from the spinning-band column was separated by gas chromatography using a Pye 105 chromatograph employing a 9.1 m × 9.5 mm column packed with PEGA 10% on Chromosorb at 60 °C to yield (i) hexadecafluorobicyclo[4,4,0]deca-1(6)-ene (I) (0.68 g), b.p. 126 °C, identical to an authentic sample; (ii) tetradecafluorobicyclo[4,4,0]-deca-1(6),3(4)-diene (II) (0.09 g). b.p. 109 °C, (Found: C, 31.2; F, 68.9%; mol. wt., 386. $C_{10}F_{14}$ requires C, 31.1; F, 68.9%; mol. wt., 386); and (iii) 3*H*-pentadecafluorobicyclo[4,4,0]deca-1(6)-ene (III) (0.39 g), b.p. 138 °C, (Found: C, 29.5; F, 70.4%; mol. wt., 406. $C_{10}HF_{15}$ requires C, 29.6; F, 70.2%; mol. wt., 406).

Dehydrofluorination of 3H-*pentadecafluorobicyclo[4,4,0]deca-1(6)-ene (III)*

The olefin (1 g) in water (1 cm^3) containing potassium hydroxide (1 g) was heated under reflux for 30 min to give a mixture shown by GLC to consist of two product peaks and some unreacted starting material. Separation by GLC afforded (i) tetradecafluorobicyclo[4,4,0]deca-1(6),3(4)-diene (II)

(0.3 g) identical to the material isolated from the fluorination above; (ii) tetradecafluorobicyclo[4,4,0]deca-1(6),2(3)-diene (IV) (0.2 g), b.p. 102 °C, (Found: C, 31.4; F, 69.1%; mol. wt., 386); UV (EtOH) $\lambda_{max.}$ 274 nm ϵ 3400 (conjugated C═C); and (iii) unreacted starting material (III) (0.3 g).

Acknowledgements

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