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POLYFLUOROBICYCLO[2, 2, 2]OCTANES. PART II. SYNTHESES OF POLYFLUOROBICYCLO[2, 2, 2]OCT-2-ENES FROM POLYFLUOROCYCLOHEXA-1, 3-DIENES

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SUMMARY

Diels-Alder reactions between ethylene and octa-, 1*H*-hepta-, and 1H, 4H-hexa-fluorocyclohexa-1, 3-diene gave, respectively, 1, 2, 3, 4, 5, 5, 6, 6-octa-, 1, 2, 3, 5, 5, 6, 6-hepta-, and 2, 3, 5, 5, 6, 6-hexafluorobicyclo[2, 2, 2]oct-2-ene, each characterised by oxidation to the corresponding polyfluorocyclohexane-1, 4-dicarboxylic acid.

INTRODUCTION

Following our work [1] on highly fluorinated bicyclo[2, 2, 1] heptanes (norbornanes), the fluorobicyclo[2, 2, 2]octane series also merited study [2]. However, the standard synthetic approach, reaction of the appropriate hydrocarbon with cobaltic fluoride [3], was not really suitable in this series. Rearrangements occur in fluorinations of bridged ring systems [4] and mixed fluorocarbon products of different carbon skeletons result. Rearrangements almost certainly occur when bicyclo[2, 2, 1]heptanes are fluorinated, but in the case of the readily-available norbornadiene itself, such rearrangements merely re-form the same basic skeleton, so that no special problems arise. With bicyclo[2, 2, 2]octane, however, different skeletons are formed, and fluorination of hydrocarbons is a poor entry to this polyfluoro-series.

In fact, bicyclo[2, 2, 2]octane is not readily available commercially and has to be made via a Diels-Alder reaction using cyclohexa-1, 3-diene. We felt therefore that not only would it be as easy to apply Diels-Alder reactions to some of our available polyfluorocyclohexa-1, 3 dienes, but partly-fluorinated bicyclo-octanes would probably undergo much less skeletal rearrangement when fluorinated further. For our preliminary studies [2], we used methyl acrylate as the dienophile, since carboxyl functions were then thought not to survive exhaustive fluorination. In fact, this was shown later [5] to be not completely true. Nevertheless, further fluorination of our carbomethoxy bicyclo-octenes did give the desired products which were isolated, though some rearrangement occurred and yields were not very good [2]. Accordingly we now report efficient Diels-Alder reactions between three fluorocyclohexadienes and ethylene, carried out some years ago, and which gave more suitable starting materials for further fluorination studies.

RESULTS AND DISCUSSION

The Diels-Alder reaction has been applied to many fluoro-enes and -dienes [6]. Successful reactions were carried out between several fluorocyclohexa-1, 3-dienes and a range of dienophiles by Musgrave, Feast, et al [7] and some useful general syntheses achieved from certain of the primary products.

Our major objectives were fluoro-bicyclo-octanes with bridgehead hydrogens, and our starting materials were three cyclohexa-1, 3-dienes, made earlier in our work on polyfluorocyclohexanes, the octafluoro-[8], 1H-heptafluoro-[9] and 1H, 4H-hexafluoro-compounds [10]. The last diene was best made by dehydrofluorination using aqueous KOH of 1H:3H/4H-heptafluorocyclohex-1-ene [11], of which we had considerable quantities available from large-scale fluorinations of benzene by potassium tetrafluorocobaltate(III).

Further, slightly different dehydrofluorination conditions than those used previously [11] were adopted and the diene obtained in better yields.

The octa-, hepta-, and hexa-fluorocyclohexadienes were reacted with ethylene for 24 h at 60-80 atm pressure in autoclaves. The best reaction temperatures were around 165°, 200° and 280°, respectively, a demonstration of inverse electron demand. The solid products, respectively 1,2,3,4,5,5,6,6-octa-, 1,2,3,5,5,6,6-hepta- and 2,3,5,5,6,6-hexa-fluorobicyclo[2,2,2]oct-2-ene had the anticipated spectroscopic properties. The first was identical with that from a similar reaction at 200°, reported [12] since the work was done.

Each bicyclo-octene was oxidised with potassium permanganate in acetone to give the appropriate cyclohexane-cis-1,4-dicarboxylic acid, respectively the 1,2,2,3,3,4-hexafluoro-, 1,2,2,3,3-pentafluoro-, and 2,2,3,3-tetrafluoro-derivatives. With diazomethane, these acids gave dimethyl esters, each with the anticipated spectroscopic properties. Undecafluorocyclohexane carboxylic acid has long been known to undergo ready decarboxylation [13], and it was of interest to find that these partly-fluorinated acids were sufficiently stable to be isolated, even though the two with fluorine on a carboxyl-carrying carbon decomposed fairly readily, particularly near their melting points.

The ultimate objectives of this work were realised when fluorination of the three fluorobicyclo-octenes gave, with no detected skeletal rearrangements, a range of polyfluorobicyclo[2,2,2]octanes, including the 1*H*- and 1*H*,4*H*-derivatives: these will be described subsequently [14].

EXPERIMENTAL

Spectroscopy

Infrared spectra were measured on a Perkin Elmer 257 grating instrument with sodium chloride optics, and mass spectra on an A.E.I. M.S.9 instrument. Nuclear magnetic resonance spectra were taken in $CC\ell_4$ solution (unless otherwise stated) using a

Varian H.A. 100 Spectrometer, ^{19}F measurements at 94.07 mHz using $CC\ell_3F$ as internal standard, and ^1H spectra at 100 mHz with $Si(Me)_4$ as internal standard, chemical shifts being quoted in ϕ^* ppm and δ ppm respectively.

1, 2, 3, 4, 5, 5, 6, 6-Octafluorobicyclo[2, 2, 2]oct-2-ene

Preparation

Octafluorocyclohexa-1,3-diene (24.9 g) and hydroquinone (0.1 g) were introduced into a 1 litre autoclave which was pressurised to ca. 80 atm with ethylene. The autoclave was rocked and maintained at 165° for 24 h then cooled, when the pressure of ethylene had dropped to ca. 60 atm. A cream crystalline solid (20 g) was obtained, a portion (2.0 g) of which was purified by sublimation under reduced pressure and recrystallisation from carbon tetrachloride to yield 1, 2, 3, 4, 5, 5, 6, 6-octafluorobicyclo [2, 2, 2]oct-2-ene (1.2 g) m.p. (sealed tube*) 105° (Found: C, 38.1; H, 1.8; F, 60.0. Calc. for $C_8H_4F_8$: C, 38.1; H, 1.6; F, 60.3%): m/e 252 (M), 152 $(M-C_2F_4)$: ^{19}F nmr, singlet 198.0 $(-\overset{|}{\underset{|}{C}}-F \times 2)$, singlet 150.5 $(=\underset{|}{C}F \times 2)$, collapsed AB quartet centred at 128.0 $(>CF_2 \times 2)$: ^1H nmr, AB quartet -2.09 and -2.33, J_{AB}=9Hz: ir 1755 cm^{-1} (-CF=CF-). The cited [12] m.p. was 98-99°.

Oxidation

The olefin (2.8 g) in acetone (10 cm^3) was added dropwise to vigorously stirred potassium permanganate (4.0 g) in acetone (65 cm^3); the heat of reaction caused the acetone to reflux. When the addition was complete the mixture was refluxed for 30 min, cooled, and water (50 cm^3) and 4N H_2SO_4 (5 cm^3) added. The acetone was removed at diminished pressure (ca 20 mm) and the residual liquid decolourised with sulphur dioxide and extracted continuously with ether for 16 h. The ether solution was dried ($MgSO_4$) and

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*Sealed tube with minimal unfilled space above the sample.

evaporated to leave a viscous liquid (2.8 g) which crystallised on standing to give a white crystalline solid. A portion of this (1.0 g) was recrystallised from benzene to yield 1,2,2,3,3,4-hexafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (0.6 g) mp 140-5° (decomp) (Found: C, 34.3; H, 2.3; F, 40.6. $C_8H_6F_6O_4$ requires C, 34.3; H, 2.2; F, 40.7%).

A portion (0.5 g) of the purified acid was dissolved in ether (5 cm^3) and an excess of diazomethane in ether (prepared from N-methyl - N - nitrosotoluene-p-sulphonamide) added. A brisk evolution of nitrogen occurred. The excess of diazomethane was allowed to evaporate during 16 h and the remaining ether solution was filtered and evaporated to a white crystalline solid (0.5 g) which was recrystallised from methanol to give the dimethyl ester of 1,2,2,3,3,4-hexafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (0.3 g) mp 74° (Found: C, 38.6; H, 3.1; F, 37.3. $C_{10}H_{10}F_6O_4$ requires C, 39.0; H, 3.3; F, 37.0%): ^{19}F nmr, singlet 177.0 (-$\underset{|}{\overset{|}{C}}$F x 2), AB quartet 129.0, 130.0, J_{AB} = 235 Hz: ^1H nmr, singlet -3.8 (CH_3 x 2), complex band centred at -2.8 (>CH_2 x 2): ir 1755 cm^{-1} (>C=O).

1,2,3,5,5,6,6-Heptafluorobicyclo[2,2,2]oct-2-ene

Preparation

1H-Heptafluorocyclohexa-1,3-diene (19.0 g) and hydroquinone (0.1 g) in a 1 litre autoclave were treated with ethylene (initial pressure 60 atm) at 200° for 24 h (pressure then ca 55 atm). A white crystalline solid (20.6 g) was obtained, a portion of which (1.5 g) was purified by sublimation under reduced pressure and recrystallised from carbon tetrachloride to yield 1,2,3,5,5,6,6-heptafluorobicyclo[2,2,2]oct-2-ene (nc) (0.8 g) mp (sealed tube*) 113° (Found: C, 41.3; H, 2.3; F, 56.9. $C_8H_5F_7$ requires C, 41.0; H, 2.1; F, 56.8%): m/e 234(M), 215(M-F), 134(M-C_2F_4): ^{19}F nmr, singlet 205.0 (-$\underset{|}{\overset{|}{C}}$-F); singlet 155.0 (=$\underset{|}{C}$F); singlet 140.0

(=$\overset{|}{\underset{|}{C}}$F); two similar AB quartets at 132.0, 130.0, 117.0, 115.0; J_{AB} = 225 Hz for each (>CF_2 x 2): ^{1}H nmr (1$\underline{M}$ in CCl_3F) -3.08 (-$\overset{|}{\underset{|}{C}}$-H), complex band centred at -2.0 (>CH_2 x 2): ir 1759 cm^{-1} (-CF=CF-).

Oxidation

The olefin (1.1 g) in acetone (10 cm^3), and potassium permanganate (3.0 g) in acetone (50 cm^3), were treated as before, and water (100 cm^3) and 4$\underline{\underline{N}}$ H_2SO_4 (10 cm^3) added. Work up as before gave a viscous liquid (1.0 g) which eventually crystallised. A portion (0.5 g) of this was recrystallised from chlorobenzene to yield 1,2,2,3,3-pentafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (0.25 g) mp 125-135° (decomp). (Found: C, 35.4; H, 2.9; F, 35.0. $C_8H_7F_5O_4$ requires C, 36.6; H, 2.7; F, 36.2%).

The purified acid (0.2 g) was dissolved in ether (3 cm^3) and an excess of diazomethane in ether added. The excess of diazomethane was allowed to evaporate over a period of ca 16 h and further evaporation gave a clear mobile liquid (0.3 g) which was distilled from P_2O_5 in vacuo to give an oil, the dimethyl ester of 1,2,2,3,3-pentafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (0.2 g) (Found: C, 41.4; H, 3.6; F, 32.9. $C_{10}H_{11}F_5O_4$ requires C, 41.4; H, 3.8; F, 32.7%): ^{19}F nmr, complex multiplet 175.0 (-$\overset{|}{\underset{|}{C}}$-F), collapsed AB quartet centred at 130.2 (>CF_2); AB quartet 122.0, 114.0; J_{AB}=260 Hz (>CF_2): ^{1}H nmr (1$\underline{M}$ in CCl_3F) singlet -3.73 (CH_3), singlet -3.85 (CH_3); complex -2.1 (5H): ir 1755 cm^{-1} (>C=O).

1H,4H-Hexafluorocyclohexa-1,3-diene

Preparation

1$\underline{\underline{H}}$:3$\underline{\underline{H}}$/4H-Heptafluorocyclohex-1-ene (35 g), potassium hydroxide (50 g) and water (50 cm^3) were refluxed carefully for 3 h. The fluorocarbon layer (31.5 g) was separated from the dark brown aqueous layer and the former shown by analytical gas phase chromatography (dinonyl phthalate/Celite 1:2; 70°; nitrogen flow-rate 6.8) to contain three components which were separated on a preparative scale (column 75 mm dia x 488 mm length, packed with dinonyl phthalate/Celite 1:2; 90°; N_2 65 l/hr) to give: (i) 1$\underline{\underline{H}}$,4$\underline{\underline{H}}$-hexafluorocyclohexa-1,3-diene (15.0 g); (ii) pentafluorobenzene (7.0 g); (iii) an impure mixture (1.9 g), containing a high proportion of an unsaturated fluorocarbon, not examined further. Fractions (i) and (ii) had correct ir spectra.

2,3,5,5,6,6-Hexafluorobicyclo[2,2,2]oct-2-ene

Preparation

1$\underline{\underline{H}}$,4$\underline{\underline{H}}$-Hexafluorocyclohexa-1,3-diene (15.0 g) and hydroquinone (0.1 g) were introduced into an autoclave (capacity 50 cm^3) pressurised to ca 60 atm with ethylene. After 24 h at 280° (pressure then ca 50 atm) a cream crystalline solid (11.1 g) was obtained. A portion (1.8 g) was purified by sublimation under reduced pressure (ca 20 mm) and recrystallised from methanol to yield 2,3,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (nc) (1.0 g) mp (sealed tube*) 114-5° (Found: C, 44.0; H, 2.8; F, 52.6. $C_8H_6F_6$ requires C, 44.4; H, 2.8; F, 52.7%): $\underline{m}/\underline{e}$ 216(M), 116($M-C_2F_4$): ^{19}F nmr, singlet 139.2 ($=\overset{|}{C}-F$ x 2); AB quartet 115.0, 110.0, J_{AB} = 235 Hz ($>CF_2$ x 2): ^1H nmr, broad band centred at -3.1 ($-\overset{|}{\underset{|}{C}}-H$ x 2), AB quartet -1.72, -1.98; J_{AB} = 10 Hz ($>CH_2$ x 2); ir 1751 cm^{-1} (-CF=CF-).

Oxidation

The olefin (2.0 g) in acetone (5 cm^3) and potassium permanganate (4.0 g) in acetone (60 cm^3), after reaction and work-up as before, gave a viscous liquid (2.5 g) which crystallised after 16 h at 0.1 mm over silica gel. Treatment with activated charcoal in boiling water and recrystallisation from chlorobenzene gave 2,2,3,3-tetrafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (1.9 g) mp 146°

(Found: C, 39.0; H, 3.4; F, 31.0. $C_8H_8F_4O_4$ requires: C, 39.3; H, 3.3; F, 31.1%).

A portion (0.5 g) of the purified acid in ether (3.0 cm^3) was treated with excess diazomethane as before giving a pale yellow oil (0.5 g) which was distilled from P_2O_5 under vacuum to yield an oil, the dimethyl ester of 2,2,3,3-tetrafluorocyclohexane-cis-1,4-dicarboxylic acid (nc) (Found: C, 43.8; H, 4.6; F, 27.8. $C_{10}H_{12}F_4O_4$ requires: C, 44.1; H, 4.4; F, 27.9%): ^{19}F nmr, AB quartet 124.0, 116.0; J_{AB} = 260 Hz, J=15 Hz (>CF_2): ^1H nmr, singlet -3.7 (R.I.1)complex band centred at -2.5 (R.I. 1): ir 1740 cm^{-1} (>C=O).

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