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POLYFLUOROCYCLOALKENES.

PART XVI [1]. SOME ADDITION REACTIONS OF 1-TRIFLUOROMETHYLNONAFLUOROCYCLOHEX-1-ENE

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SUMMARY

Reactions with alcohols and base replaced the vinylic fluorine of 1-trifluoromethylnonafluorocyclohex-1-ene(I) by methoxy and ethoxy groups. Fluorination with cobaltic fluoride gave, from the former, a number of saturated polyfluoro-ethers. Oxidation of the alkoxy-cycloalkenes gave hexafluoroglutaric acid. Cycloalkene I gave with ammonia an imino-enamine, which was hydrolysed by dilute acid to a keto-enamine. I was defluorinated by heated iron to octafluorotoluene.

INTRODUCTION

We recently gave the full experimental details for some early work on the fluorination of benzotrifluoride by cobaltic fluoride, to give six trifluoromethyldecafluorocyclohexanes [2]. Dehydrofluorinations of the two 2H-isomers gave 1-trifluoromethylnonafluorocyclohex-1-ene(I), and this note reports a few of its addition reactions.

RESULTS

Methanol and ethanol in the presence of potassium hydroxide gave from I, respectively, 1-methoxy-(II) and 1-ethoxy-(III)-2-trifluoromethyl-octafluorocyclohex-1-ene. Only one product in each case was shown up by glc. The structures were established by the presence of four groups of peaks of correct relative intensity in the ^{19}F nmr spectrum corresponding

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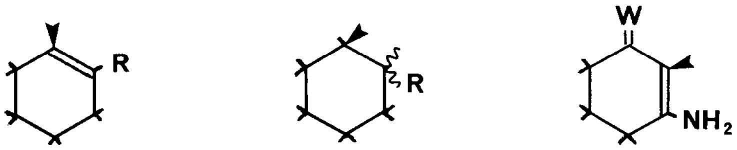
to CF_3 and four CF_2 groups, with no vinylic fluorine. Oxidation of the alkoxy-cycloalkenes(II and III) afforded hexafluoroglutaric acid in each case, characterised as the dianilinium salt. An explanation for the formation of this acid from olefins with a vinylic CF_3 group has been advanced already [2].

Fluorination of the methoxy-compound(II) over cobaltic fluoride at 70°, gave a mixture of five saturated ethers and a little starting material. The products included the difluoro-adducts, the saturated ethers,cis-(IV) and trans-(V)-1-methoxy-2-trifluoromethyldecafluorocyclohexanes. Further fluorination of the methoxy groups also occurred, the cis-(VI) and trans(VII)-1-fluoromethoxy-analogues, and one of the 1-difluoromethoxy-analogues(VIII) were also present. Structure proof was by ^1H and ^{19}F nmr [cf. 3], the cis-isomers each having a peak at around 70 p.p.m., given by an equatorial fluorine on C_1, and characteristically [4] around 20 p.p.m. higher than that from the corresponding axial position.

Olefin I with ammonia in ether gave an imino-enamine(IX), already described [5]. With dilute hydrochloric acid this was hydrolysed to the corresponding keto-enamine(X), having the expected spectroscopic parameters.

The fluoro-ene I gave octafluorotoluene when defluorinated by iron gauze at 400-500°, optimally at 440-460°. Around 14% of cyclo-alkene was recovered, with ca. 50% conversion of that which reacted.



I R=F
II R=OMe
III R=OEt

IV R=OMe cis
V R=OMe trans
VI R=OCH_2F cis
VII R=OCH_2F trans
VIII R=$OCHF_2$

IX W=NH
X W=O

▼ = CF_3

All unmarked bonds are to FLUORINE

SCHEME

DISCUSSION

The direction of addition of alcohols to the 1-trifluoromethyl-ene(I) is as expected. Initial nucleophilic attack, to locate the negative charge on the carbon bearing CF_3, followed by loss of fluoride ion to give an alkene with no vinylic fluorine,is entirely in accord with current mechanistic ideas [6]. The structure of the imino-enamine(IX) was established before [5]: the compound arises from the same point of initial attack, the process then following the pathway proposed earlier for such reactions with other fluoro-cycloalkenes [7]. Hydrolysis of the imino-function of IX, to give the keto-enamine X, is also a general process for these products of addition of ammonia to fluorocycloalkenes [7].

EXPERIMENTAL

General

Gas-liquid chromatography (glc) was as described before [2], as were spectroscopic measurements. For ^{19}F nmr [8], relative peak intensities are in brackets. ^{1}H Nmr measurements were done on a Varian A60 instrument using tetramethylsilane as internal reference.

Reactions of 1-trifluoromethylnonafluorocyclohex-1-ene(I) - I was first synthesised by Haszeldine and Osborne [9], who added chlorine and bromine to give dihalogeno-adducts, confirmed by us. No other reactions seem to have been reported since.

(a) With methanol - Dry methanol (5.0 cm^3) was added dropwise to a stirred mixture of I (15.0 g) and potassium hydroxide (3.3 g) at 15°. Heat was evolved, and,when addition was complete,stirring was continued for 1 h at ca. 50°. Excess water was added and the fluorocarbon layer separated, and dried ($MgSO_4$). Analytical glc showed only 2 peaks and preparative glc (B, 97°, 52) gave (i), I, (2.4 g): (ii), 1-methoxy-2-trifluoromethyloctafluorocyclohex-1-ene(II) nc, (8.7 g) b.p. 114° (Found: C, 29.4; H, 0.9. $C_8H_3F_{11}O$ requires C, 29.6; H, 0.9%); ir 2960 (w), 1660 (s); ^{19}F nmr, -17.6 (3), 31.9 (2), 38.2 (2), 58.5 (4).

(b) With ethanol - As in (a), using ethanol (7.0 cm^3): obtained were I (3.4 g) and 1-ethoxy-2-trifluoromethylnonafluorocyclohex-1-ene(III) nc, (7.2 g) (Found: C, 31.8; H, 1.3. $C_9H_5F_{11}O$ requires C, 32.0; H, 1.5%); ir 2990 (w), 1695 (m); ^{19}F nmr similar to II.

(c) With heated iron gauze - In four experiments, I (8.0 g) was passed over heated iron gauze (1 x 440° 2 x 450°; 1 x 500°) to give a product (4.8 g) separated by glc (A, 100°, 20) into (i), I (1.1 g): (ii), octafluorotoluene (2.6 g) [10].

Oxidation of the 1-alkoxy-2-trifluoromethyl-enes(II and III) - II (1.0 g), potassium permanganate (10.0 g) and acetone (200 cm^3) were shaken together for 30 min. Isolation as usual gave dianilinium hexafluoroglutarate (0.67 g) m.p. 219°, correct ir [11].

The analogous reaction with III gave the same salt in similar yield.

Fluorination of the 1-methoxy-2-trifluoromethyl-ene(II) - Passage of II (4.0 g) in a stream of nitrogen (5 ℓ h^{-1}) through a small stirred cobalt fluoride reactor [2] at 70°, gave a product : glc separation (A, 100°, 16) gave:- (i), 1-difluoromethoxy-2-trifluoromethyldecafluorocyclohexane(VIII) nc, (0.3 g) (Found: C, 24.3; H, 0.15. $C_8HF_{15}O$ requires C, 24.1; H, 0.25%); ^1H nmr 6.4 (t, J=68): (ii), cis-1-methoxy-2-trifluoromethyldecafluorocyclohexane(IV) nc (0.9 g) (Found: C, 26.5; H, 0.6. $C_8H_3F_{13}O$ requires C, 26.5; H, 0.8%); ir 3000 (w); ^1H nmr 3.5 (d, J=4); ^{19}F nmr -7 (3), 35-60 (8), 70 (equ. F on C_1) (1), 105 (axial F on C_2) (1): (iii), trans-1-methoxy-2-trifluoromethyldecafluorocyclohexane(V) nc, (0.4 g) (Found: C, 26.6; H, 0.9%); ir 3000 (w); ^1H nmr 3.4 (b); ^{19}F nmr, similar to IV but no band at 70 and those at 35-60 with relative intensity 9 (axial F ca. 20 p.p.m. lower than equatorial [4]): (iv), trans-1-fluoromethoxy-2-trifluoromethyldecafluorocyclohexane(VII) nc, (0.8 g) (Found: C, 24.8; H, 0.4. $C_8H_2F_{14}O$ requires C, 25.3; H, 0.5%); ir 3000 (w); ^1H nmr 5.4 (bd, J=50); ^{19}F nmr -7.5 (3), 40-65 (9), 75 (ct,OCH_2F)(1), 110 (axial F on C_2)(1): (v), cis-1-fluoromethoxy-2-trifluoromethyldecafluorocyclohexane(VI) nc, (0.3 g) (Found: C, 25.2; H, 0.5%); ir 3000 (w); ^1H nmr 5.3 (d, J=50); ^{19}F nmr, similar to VII, but the 40-65 peaks had relative intensity 8, and there was a singlet at 70 (equ. F on C_1) (1): (vi), recovered II (0.5 g), by ir.

Hydrolysis of 1-amino-3-imino-2-trifluoromethylhexafluorocyclohex-1-ene(IX) - IX (2.0 g) was shaken with hydrochloric acid (70 cm^3; 2M) until it had dissolved, and the mixture was kept at 20° for 2 h by which time a precipitate had formed. After cooling and filtration, the solid was dried in vacuo (1.2 g) and recrystallised from carbon tetrachloride to give 1-amino-2-trifluoromethylhexafluorocyclohex-1-ene-3-one(X) nc, m.p. 97° (Found: C, 28.9; H, 0.7; N, 4.7. $C_7H_2F_9NO$ requires C, 29.3; H, 0.7; N, 4.9%); ir 1660 (shoulder), 1625 (s), 1585 (s); UV λ 2800 A (ε 2.8 x 10^4, conc. 0.1 mg/cm^3 in ethanol).

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