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SOME REACTIONS OF DIAZOMETHANE WITH POLYFLUOROAZAOLEFINS

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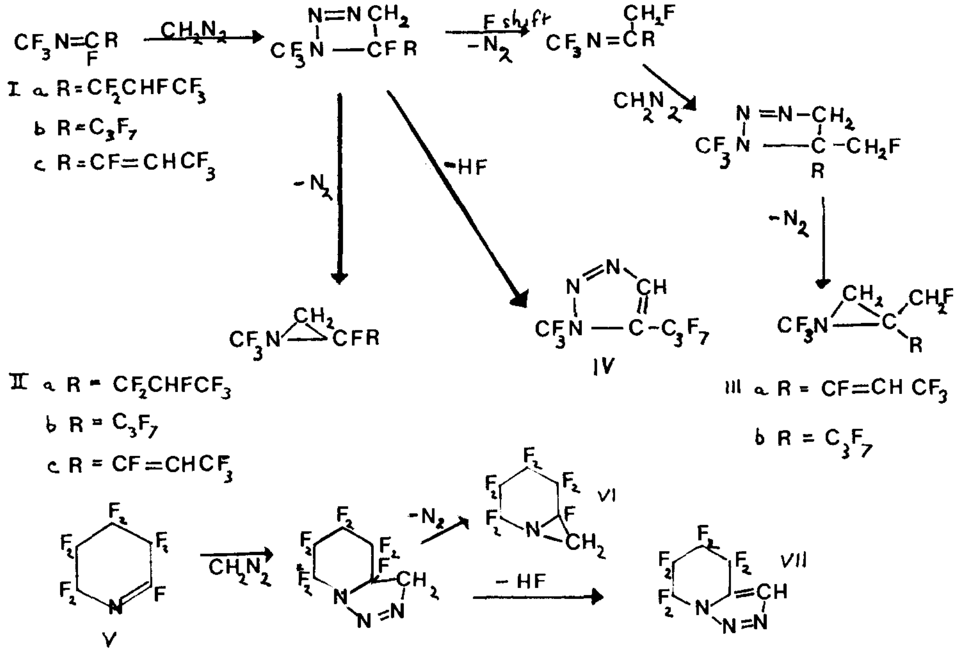
SUMMARY

The reactions of some polyfluoroazaolefins with diazomethane are described. Thus 5-H-decafluoro-2-aza-hex-2(Z)-ene yields 1-trifluoromethyl-2-fluoro-2-(1, 1, 2, 3, 3, 3-hexafluoropropyl)-aziridine as the sole isolable product. However, undecafluoro-2-azahex-2(Z)-ene yields not only the corresponding aziridine, 1- trifluoromethyl-2-fluoro-2-(heptafluoropropyl) aziridine, but also 1-trifluoromethyl-5-(heptafluoropropyl)-1, 2, 3-triazole, and 1-trifluoromethyl-2-fluoromethyl-2-(heptafluoropropyl) aziridine. 5-H-octafluoro-2-azahexa-2(Z)4(Z)-diene yielded the expected aziridine and 1-trifluoromethyl-2-fluoromethyl-2-(1, 1, 3, 3-tetrafluoroprop-2-enyl) aziridine. No products were observed as a result of reactions at the C = C bond and no triazole was isolated in this case. Nonafluoroazacyclohex-1-ene gave the corresponding aziridine and a small amount of a compound believed to be 2, 2, 3, 3, 4, 4, 5, 5-octafluoro-1, 8, 9-triazabicyclo [4, 3, 0] nonadiene i. e. the triazole product.

INTRODUCTION

The dipolar addition of diazoalkanes to suitably activated olefins has been well established in the hydrocarbon field for many years, and the subject reviewed by Huisgen [1]. Dipolar addition to fluoroolefins has however received little attention and there are but few examples of addition to fluoro imines. Perfluoroacetone imine is reported [2] to give a triazoline as the initial adduct which decomposes on treatment with concentrated acid to give 1-fluoro-2, 2-bis(trifluoromethyl) aziridine. Reaction of perfluoro-2-azapropene with diazomethane gave 1-trifluoromethyl-2, 2-difluoroaziridine as the sole product. No evidence was found for insertion into C-F bonds, but there have been cases observed where insertion takes place into C-Cl bonds [3].



RESULTS AND DISCUSSION

We now report the reaction of diazomethane with some azaalkenes obtained from the fluorination of pyridine with $KCoF_4$ [4]. Thus treatment of 5H-decafluoro-2-azahex-2(Z)-ene (Ia) with excess diazomethane in ether afforded 1-trifluoromethyl-2-fluoro-2-(1, 1, 2, 3, 3, 3-hexafluoropropyl) aziridine (IIa) and no other product could be detected. The structure of the aziridine was indicated by elemental analysis, mass spectrometry and particularly ^{19}F and ^{1}H n.m.r. spectroscopy. The product contains two chiral centres and we would thus expect four diasteroisomers and indeed the ^{19}F n.m.r. spectrum clearly showed the presence of two distinct signals for the 2-fluorine atom, the difluoromethylene and the side chain monofluoromethylene groups respectively. The integral ratio of the peaks suggests a 50:50 mixture of the two enantiomeric pairs. None of the g.l.c. columns available to us however, were able to resolve the pairs of isomers.

Reaction of 5H-octafluoro-2-azahexa-2(Z)4(Z)-diene (Ic) with diazomethane as above yielded a mixture of two products in the ratio 71:29. The principal product was shown by ^{19}F and ^{1}H n.m.r. spectroscopy, elemental analysis and mass spectrometry to be 1-trifluoromethyl-2-fluoro-2-(1, 3, 3, 3-tetrafluoroprop-(Z)-enyl) aziridine (IIc). The second product showed many similar features to (IIc) in its various spectra but the mass spectrum indicated the presence of an extra CH_2 group. The position of this group was resolved by ^{1}H n.m.r. spectroscopy, which showed an AB system on which was superimposed a large doublet coupling of 47 Hz, characteristic of a geminal H-F coupling. These data would suggest that there has been a CH_2 insertion into a CF bond to form a CH_2F group. This is in accord with the remaining spectral details and indicates the product to be 1-trifluoromethyl-2-fluoromethyl-2-(tetrafluoroprop-(Z)-enyl)-aziridine (IIIa).

Reaction of undecafluoro-2-azahex-2(Z)-ene (Ib) with excess diazomethane gave a mixture of three components in the ratio 6:9:1 by g.l.c. analysis. The first component was indicated by mass spectrometry and [redacted] nitrogen, a single CF group, the expected signals for C_3F_7 group and a CH_2 group. These data suggest the product to be the simple CH_2: adduct across the C = N bond i.e. 1-trifluoromethyl-2-fluoro-2-(heptafluoropropyl) aziridine (IIb). The second component of the mixture was shown by elemental analysis and mass spectrometry to be $C_6HF_{10}N_3$. The presence of three nitrogen atoms in the molecule suggest a dipolar addition across the -C = N- bond. ^{1}H n.m.r. spectroscopy showed the presence of a single olefin proton at 1.98, the signal being a very broad singlet. ^{19}F n.m.r. showed the presence of a CF_3 group attached to nitrogen and a heptafluoropropyl group but no signal for a tertiary fluorine atom. The i.r. spectrum showed a strong band at 1545 cm^{-1} attributable to a C = C double bond, probably in a ring. These data suggest the component to be 1-trifluoromethyl-5-(heptafluoropropyl)-1, 2, 3-triazole (IV). The third component of the reaction mixture, in very small yield, showed ^{1}H and ^{19}F n. m. r. spectra which indicated the presence of CF, C_3F_7 and CH_2F groups, no tertiary fluorine signal was again observed. The i. r. spectrum showed no unsaturation to be present and the mass spectrum was consistent with the product being 1-trifluoromethyl-2-fluoromethyl-2-(heptafluoropropyl) aziridine (IIIb).

The reaction of diazomethane with nonafluoroazacyclohex-1-ene (V) gave a two product mixture the product ratio being 10:1. G. l. c. separation afforded two liquid products. The major component had elemental analysis and mass spectral data consistent with an empirical formula of $C_6H_2F_9N$ i. e. the CH_2 addition product. ^{1}H n. m. r. spectroscopy showed broad peaks at 7. 15 and 7. 45 τ in the integral ratio 1:1 and the ^{19}F spectrum in addition to AB type signals for four CF_2 groups showed a signal at ϕ 164. 3, a broad singlet attributable to a tertiary fluorine atom. These data indicate the product to be 2, 2, 3, 3, 4, 4, 5, 5, 6-nonafluoro-1-azabicyclo [4. 1. 0] heptane (VI) i. e. the CH_2 "adduct" similar to those obtained with acyclic olefins. The second and very minor product was indicated by mass spectrometry to contain three nitrogen atoms. The ^{1}H n. m. r. spectrum showed a broad singlet at 1. 84 τ and the ^{19}F spectra showed only signals for four CF_2 groups, no tertiary fluorine signal could be detected. The i. r. spectrum showed a strong band at 1560 cm^{-1}, cf the band at 1545 cm^{-1} in (IV). These data suggest the compound to be 2, 2, 3, 3, 4, 4, 5, 5-octafluoro 1, 8, 9-triaza-bicyclo [4. 3. 0] nona-6, 8-diene (VII).

The route by which these compounds seem to arise fits reasonably well to pattern of products observed by Huisgen in the hydrocarbon field and is outlined in the scheme [1]. Thus the first step appears to be the 1. 3-dipolar addition diazomethane to give an intermediate of type II: the fate of this adduct seems to depend on the electronegativity of the group R. When R is strongly electro-negative, e. g. C_3F_7, all three types of product are obtained, but with CF_3CFHCF_2 and $CF_3CH = CF$-, no triazole type products are obtained. The balance between the effect of the group R appears to be very fine, cf C_3F_7 vs $CF_3CHF\ CF_2$-, and interestingly this is also reflected in the rates of hydrolysis of the starting imines [5]. At this stage it is not possible to rule out completely a carbene attack giving both the CH_2 addition and insertion reactions, but it should be stressed that the reactions were carried out under such conditions that do not normally lead to carbene formation, and further in the case when (Ic) was the starting material no addition to the C = C bond was observed, and if carbenes were present some reaction at this bond might have been expected.

EXPERIMENTAL

Reaction of 5H-decafluoro-2-azahexa-2(Z)-ene with diazomethane

Diazomethane ether azeotrope (from N-nitroso-N-methyl p-toluene-sulphonamide 5 g) was distilled into a solution of 5H-decafluoro-2-azahex-2(Z)-ene (2 g) in dry ether (4 cm^3) at 0°. Nitrogen was evolved and the distillation was continued until a permanent yellow colour was established. The resulting mixture was allowed to stand at 0° for 1 h and then the excess ether diazomethane were distilled off through a 15 cm glass helix packed column to a final volume of ca 3 cm^3. The residue was distilled in vacuo to a colourless liquid which was shown to contain ether and another component by analytical g.l.c. Separation by semi-preparative g.l.c. (10% Kel F oil on chromasorb 9.2 m x 9 mm at 80° 15 p.s.i. N_2) gave (i) ether (ii) 1-trifluoromethyl-2-fluoro-2-(1, 1, 2, 3, 3, 3-hexafluoropropyl)-aziridine (nc) (1.4 g) b.p. 102 - 103. (Found: C, 26.1; H, 1.3; F, 68.2 M (mass spec) 279 $C_6H_3F_{10}N$ requires C, 25.8; H, 1.1; F 68.1% M. 279).

Reaction of 5H-octafluoro-2-azahexa-2(Z), 4(Z) diene with diazomethane

In a similar experiment to that above, reaction of diazomethane (from N-nitro-N-methyl p-toluene sulphonamide10 g) with 5H-octafluoro-2-azahexa-2(Z), 4(Z)-diene (4.0 g) afforded a mixture of three components in the ratio (7, 5, 2) which were separated, as above, by preparative g.l.c. to give (i) ether (ii) 1-trifluoromethyl-2-fluoro-2-(1, 3, 3, 3-tetrafluoro-prop-(Z)-enyl)-aziridine (nc) (2.1 g) b.p. 109 - 110°. (Analysis: Found: C, 29.7; H, 1.2; F, 62.9; M 241 $C_6H_3F_8N$ requires C, 29.8; H, 1.2;

F, 63.0% M 241) and (iii) 1-trifluoromethyl-2-fluoromethyl-2-(1, 3, 3, 3-tetrafluoro prop-(Z)-enyl)-aziridine (nc) (0.8 g) b.p. 146° (Analysis: Found: C, 32.6; H, 2.1; F, 59.3; M-F. 236 $C_7H_5F_8N$ requires C, 32.9; H, 1.9; F, 59.6% M-F 236).

Reaction of undecafluoro-2-azahex-2(Z)-ene with diazomethane

In a similar manner undecafluoro-2-azahex-2(Z)-ene (2.0 g) afforded three components in the ratio 6:9:1 by g.l.c. analysis which were separated to give (i) 1-trifluoromethyl-2-fluoro-2-(heptafluoropropyl) aziridine (nc) (0.72 g) b.p. 86-87° (Analysis: Found: C, 24.1; H, 0.8; F, 70.2 M 297 $C_6H_2F_{11}N$ requires C, 24.2; H, 0.7; F, 70.4%; M 297) (ii) 1-trifluoromethyl-5-(heptafluoropropyl)-1, 2, 3-triazole (nc) (1.1 g) b.p. 115-116° (Analysis: Found: C, 23.9; H, 0.5; F, 62.8; N, 12.9 M 305 $C_6HF_{10}N_3$ requires C, 23.6; H, 0.3; F, 62.3; N, 13.7% M 305) (iii) 1-trifluoromethyl-2-fluoromethyl-2-(heptafluoropropyl)-aziridine (nc) (0.12 g) b.p. 120-121° (Analysis: Found: M-F 292 requires M-F 292).

Reaction of diazomethane with nonafluoroazacyclohex-1-ene

Nonafluoroazacyclohex-1-ene (2 g) was reacted with diazomethane as above to give a mixture of one major and one minor component (ratio 10:1) which was separated by g.l.c. to give (i) 2, 2, 3, 3, 4, 4, 5, 5, 6-nonafluoro-1-azabicyclo [4, 1, 0]-heptane (nc) (1.3 g) b.p. 96-97°, (Analysis: Found: C, 27.6; H, 0.8; F, 66.0 M 259 $C_6H_2F_9N$ requires C, 27.8; H, 0.8; F, 66.1% M 259) and (ii) 2, 2, 3, 3, 4, 4, 5, 5-octafluoro-1, 8, 9-triazabicyclo [4, 3, 0] nona-6, 8-diene (nc) (0.15 g) b.p. 129-130° Analysis: (Found: M-F 248 requires M-F 248).

The ^1H and ^{19}F n.m.r. data for these compounds are given in Table 1.

TABLE 1

^1H and ^{19}F n.m.r. Data

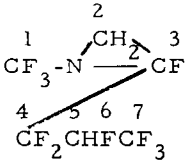
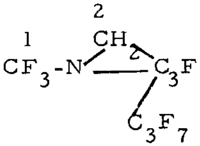
	^1H (τ)				^{19}F (ppm rel CCl_3F)			
Compound	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)
	4.94 (cd)	1	5	$J_{56} = 45$	59.7 (d)	3	1	
	7.13 (bd)	1	2	$J_d = 8.0$	74.9 (c)	3	7	
	7.40 (d)	1	2	$J_d = 4.5$	122.8 coll. AB 124.9 AB	2	4	$J_{AB} = 360$ $\Delta\nu$ 335
					188.4 189.4 (bc)	1	3	
					213.5 (dp)	1	6	$J_{56} = 45$
					215.1 (cd)	3	1	$J_d = 46$
	7.14 (bd)	1	2	$J_d = 7.5$	60.0 (d)	3	1	$J_d = 12$

TABLE 1 (CONT.)

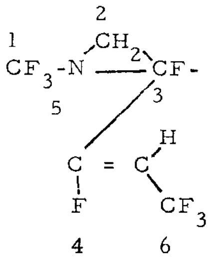
Compound	^1H (τ) Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)	^{19}F (ppm rel CCl_3F) Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)
	7.43 (d)	1	2	$J_d = 4.5$	81.8 124.0 126.8	7	C_3F_7	
					189.7 (bs)	1	3	
 $\overset{1}{CF_3}$-N(CH$_2$)CF- …	4.6 (dq)	1	5	$J_{45} = 30$	59.7 (cm)	6	1 & 6	
	7.2 (ddd)	1	2	$J_{56} = 7.5$	110.3 (bc)	1	4	
	7.35 (dd)	1	2	$J_{gem} = 1.2$	171.3 (bs)	1	3	

TABLE 1 (CONT. (2))

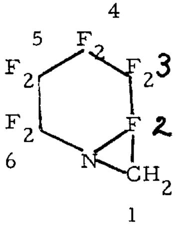
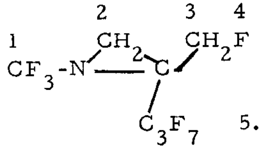
	^1H (τ)				^{19}F (ppm rel CCl_3F)			
Compound	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)
	7.15 (bs)	1	1		91.0 (AB)	2	6	J_{AB} = 228 $\Delta\nu$ 238
	7.45 (bs)	1	1		118.8 (coll AB)	2	3	
					132.2 (AB)	2	4 or 5	J_{AB} = 288 $\Delta\nu$ 290
					134.0 (AB)	2	4 or 5	J_{AB} = 300 $\Delta\nu$ 824
					164.3 (bs)	1	2	
	5.15 (d)	1	3	J_{34} = 47	59.4 (d)	3	1	J_{43} = 48

TABLE 1 (CONT. (3))

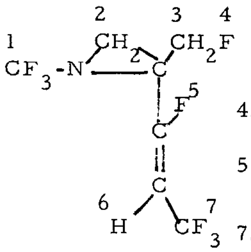
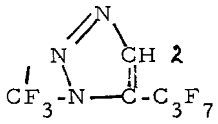
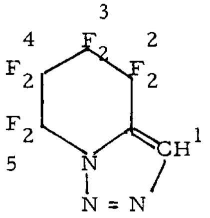
	^{1}H (τ)				^{19}F (ppm rel CCl_3F)			
Compound	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)
	7.30 (bs)	1	2		81.5 (t) 119.8 (cm) 125.8 (coll AB)	7	C_3F_7	
	7.39 (bs)	1	2		220.8 (t)	1	4	
	4.45 (dq)	1	6	J_{65} = 31 J_{67} = 7	59.2 (dd)	3	7	J_{75} = 18 J_{76} = 8
	5.34 (dAB)	2	3	J_{34} = 47 J_{AB} = 11.5 13.8	59.4 (b) 101.8 (bs)	3 1	1 5	
	7.84 (cm)	2	2		222.8 (t)	1	4	J_{43} = 49

TABLE 1 (CONT. (4))

Compound	^{1}H (τ)				^{19}F (ppm rel CCl_3F)			
	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)	Position/ signal	Rel. Int.	Assignment	Coupling constants (Hz)
	1.98 (bs)	2			57.4 (h)	3	1	
					80.7 (t)			
					105.7 (ch)	7	C_3F_7	
					125.1 (q)			
	1.84 (bs)	1			92.4 (p)	1	5	$J_p = 7.5$
					106.9 (pd)	1	2	$J_p = 8.6$ $J_{21} = 2$
					132.5 (h)	1	3 or 4	$J_h = 8$
					134.8 (h)	1	3 or 4	$J_h = 8.5$

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