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FREE-RADICAL CHEMISTRY. PART 7 [1]. ADDITIONS TO HEXAFLUORO-2-BUTYNE

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SUMMARY

Free radical additions of aldehydes and alcohols to hexafluoro-2butyne (1), using γ -ray or peroxide initiation, are described. The stereochemistry of addition appears to be determined by the steric requirements of the attacking radical. Telomers are obtained in reactions of (1) with t-butylperoxide but no co-polymers have been produced.

INTRODUCTION

A number of free-radical additions to hexafluoro-2-butyne (1) are known [2] but are essentially confined to reactions of halogens, polyfluoroiodoalkanes, and hydrogen sulphide. We are only aware of one report of addition of a functional hydrocarbon derivative <u>i.e</u>. Muramatsu [3] has claimed the addition of ethanol, to (1), in $CF_2ClCFCl_2$ as solvent and using γ -ray initiation.

RESULTS AND DISCUSSION

We now find that acetaldehyde adds to (1), either by γ -ray or peroxide, initiation. γ -Ray addition was highly selective, giving only the monoaddition product (2) and in exclusively the <u>trans</u>-form. The structure of (2) follows easily from well established values for J_{CF2-CF2} <u>cis</u> and <u>trans</u> [4].

A corresponding reaction, using benzoyl peroxide at $75^{\circ}C$ as initiator, gave a mixture of (2), together with the di-adduct (3). Clearly, the higher temperature has led to further reaction and the formation of the symmetrical isomer (3) is understandable because further attack of a radical on (2) should occur at the position in the double bond opposite to carbonyl, thereby producing a conjugated radical intermediate. However,

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 γ = Gamma-rays at room temp. B.P. = Benzoyl peroxide, 75^oC.

the situation becomes more complex with C_2H_5 CHO because, in this case, the adduct (4) was obtained together with <u>both</u> symmetrical (5) and unsymmetrical (6) isomers of the further addition product. This unexpected difference in behaviour for the two aldehydes is probably related to steric requirements but, at this time, we are unable to rationalise this effect. Reaction with C_3H_7 CHO gave a complex mixture of products that could not be separated, except for a small amount of the simple adduct. Furthermore, identification by m.s.-g.l.c. was complicated by the fact that parent peaks were not observed for the di-adducts. Nevertheless, the complexity of the product does indicate that more than one type of radical intermediate is generated from butanal in the initiation step. Crotonaldehyde gave no product and this probably stems from enhanced stability, and hence lower reactivity, of the derived radical.

In contrast to the results of Muramatsu [3] and co-workers, who used $CF_2ClCFCl_2$ as solvent, we obtained a mixture of products in the addition of neat methanol to (1). The principal product (7), however, arises from nucleophilic addition to (1); a small amount of (8) was obtained and only the <u>trans</u>-isomer could be detected. Nucleophilic attack did not compete,



however, when trifluoroethanol was used and this system gave entirely the products of radical addition; surprisingly, comparable amounts of both <u>trans</u> (9) and <u>cis</u> (10) adducts were obtained.

The stereochemistry of radical additions to hexafluoro-2-butyne (1) is interesting for comparison with results obtained for nucleophilic addition [5]. Calculations have indicated that the inversion barrier for a vinyl anion is substantially higher than for a vinyl radical [6] and, consequently, we would expect easier equilibration between intermediates in the addition of radicals to (1) than for addition of nucleophiles to (1). It seems more reasonable, therefore, to regard radical additions to (1) to be essentially under thermodynamic control, whereas we have previously argued that nucleophilic additions to (1) are essentially under kinetic control [5]. If the barrier for interconversion between the intermediate radicals (11) and (12) is low then the ratio of trans- (13) to cis- (14) products observed would depend on the equilibrium constant K. This would, of course, be wholly related to steric requirements of the radical R. and this seems to relate reasonably with our results. When R = COCH₂, <u>i.e.</u> a planar site with correspondingly low steric requirements, then (13) is obtained exclusively. A similar result is obtained with $R = CH_{2}OH$. However, when $R = CF_{2}CHOH$ then this group appears to have a steric requirement that is comparable to that of CF_3 because both (13) and (14) are obtained. It is worth noting that, although nucleophilic additions of alcohols gave, in many cases, predominantly trans-addition, in no case did we observe exclusive formation of one isomer [5].

No telomers were observed with aldehydes or alcohols and this probably reflects the efficient chain-transfer properties of these systems. Some telomeric products were obtained in a process initiated by

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tertiary butylperoxide, the initiating radical being methyl. The telomers (15) could not be separated but were easily identified by m.s.-g.l.c. Neither telomers nor adducts could be obtained in γ -ray induced reactions with (1), using CF₂Br₂, CHCl₃, CCl₄. Furthermore, no co-polymers could be obtained with either styrene or methylmethacrylate, in spite of the fact that a homopolymer of (1) may be obtained by γ -ray irradiation [7]. This is not formed in the presence of other monomers.

At this time we are unable to account for the contrasting facts that: radical additions to hexafluoro-2-butyne (1) occur; a homopolymer of (1) is formed, but co-polymerisations involving (1) have not been achieved.

$$tBu_{2}O_{2} \xrightarrow{110^{\circ}} t-Bu0^{\circ} \xrightarrow{CH_{3}} t^{CH_{3}} + CH_{3}COCH_{3}$$

$$CH_{3}^{\circ} + (1) \xrightarrow{CH_{3}[C(CF_{3}]=C(CF_{3})]_{n}^{\circ}} + \int_{Abstr.} CH_{3}[C(CF_{3})=C(CF_{3})]_{n}H$$

$$(15) \quad (n = 1-4)$$

EXPERIMENTAL

 19 F and 1 H n.m.r. spectra were recorded at 40°C using a Varian A56/ 60D spectrometer, with trichlorofluoromethane or tetramethylsilane as external reference. Upfield 19 F shifts are quoted as positive. G.l.c. was carried out on a Varian Aerograph Model 920 equipped with a gas density balance detector, using columns packed with 30% SE-30 gum rubber (column 0) or 20% di-isodecylphthalate on Chromosorb P (column A). Mass spectra were determined either on an A.E.I. MS9 mass spectrometer or V.C. Micromass 12B spectrometer linked to a gas chromatograph. Irradiation by gamma-rays was carried out as previously described [8].

Reaction of (1) with aldehydes

(a) Acetaldehyde

(i) <u>Gamma ray initiation</u>. A mixture containing acetaldehyde (5.0 g, 114 mmol) and hexafluoro-2-butyne (1) (19.7 g, 122 mmol) was irradiated to a dose of 1.1 x 10⁷ rads. Unreacted (1) (11.0 g) was recovered and the residual mixture was washed with water, the lower fluorocarbon layer removed, dried (P_2O_5) , and transferred under vacuum to a trap cooled in liquid air. The resultant liquid was shown by g.l.c. (column 0) to be a single component, identified as (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (2) (nc), (3.3 g, 30%): b.p. 88-89°C; Analysis: C, 35.1; H, 1.9; F, 55.2%; M⁺, 206. $C_6H_4F_6O$ requires: C, 34.95; H, 1.94; F, 55.34%; M, 206; v_{max} (C=0) 1720 cm⁻¹; δ_F 63.1 (3F, d, J 7.5 Hz, F_a) and 67.4 (3F, s, F_b); δ_H 2.37 (3H, s, CH₃) and 6.37 (1H, d, J 7.5 Hz, =CH).



(2)

(ii) <u>Benzoyl peroxide initiation</u>. A mixture containing acetaldehyde (5.8 g, 130 mmol), hexafluoro-2-butyne (1) (8.4 g, 52 mmol), and benzoyl peroxide (0.20 g, 0.8 mmol) was heated at 75° C for 16 h. The resulting mixture was filtered and the filtrate was shown by g.l.c. (column 0) to contain essentially one component, which was purified by preparative scale

g.l.c. and identified as (2) (1.9 g, 18%). The solid product was recrystallised from chloroform to give 3,4-bistrifluoromethylhexa-2,5-dione (3) (nc) (6.0 g, 46%): m.p. 122-123°C; Analysis: C, 38.4; H, 3.2; F, 45.6%; M⁺, 250. $C_8H_8F_6O_2$ requires: C, 38.68; H, 3.01; F, 45.20%; M, 250; v_{max} (C=0) 1720 cm⁻¹; δ_F (CDCl₃) 63.9 (s, CF₃); δ_H 2.4 (3H, s, CH₂) and 4.1 (1H, s, >CH).

(b) Propanal

A mixture containing propanal (2.2 g, 38 mmol), hexafluoro-2-butyne (7.4 g, 46 mmol), and benzoyl peroxide (0.20 g, 0.8 mmol) was heated at 75°C for 16 h. A liquid (2.9 g), a white solid (3.4 g), and (1) (3.1 g) were recovered. The liquid was distilled to give (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (4) (nc) (2.3 g, 40%): b.p. 93-4°C; Analysis: C, 38.3; H, 2.8; F, 51.6%; M^+ , 220; v_{max} (C=0) 1725 cm⁻¹; $\delta_{\rm F}$ 63.0 (3F, dq, J 7 and 1.6 Hz, $F_{\rm A}$) and 67.3 (3F, broad s, $F_{\rm h}$); $\delta_{\rm H}$ 1.08 $(3H, t, J 7 Hz, CH_{2})$, 2.69 (2H, q, J 7 Hz, CH₂), and 6.40 (1H, qq, J 7 and 1.3 Hz, CH). The solid was sublimed under vacuum to give white crystals (3.4 g), which were identified as a mixture of 4,5-bistrifluoromethylocta-3,6-dione (5) (nc) and 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (6) (nc) in the ratio of 88:12. The yields of (5) and (6) were calculated as 41 and 6%, respectively. For the mixture of (5) and (6): Analysis: C, 42.9; H, 4.2; F, 40.6%; M^+ , 278. $C_{10}H_{12}F_6O_2$ requires: C, 43.16; H, 4.32; F, 41.01%; M, 278; v_{max} 1730 cm⁻¹. For compound (5): $\delta_{\rm F}$ (CDCl₃) 64.2 (broad m, CF₃); $\delta_{\rm H}$ 1.13 (3H, broad m, CH₂), 2.68 (2H, broad q, CH_2), and 4.08 (1H, broad s, >CH). For compound (6): δ_F (CDCl₂) 60.2 (3F, broad s, F_a) and 69.6 (3F, broad s, F_b); δ_H 1.13 (3H, broad m, CH_3) and 2.68 (2H, broad q, CH_2).



(c) <u>Butanal</u>

A mixture containing butanal (3.2 g, 44 mmol), hexafluoro-2-butyne (1) (10 g, 62 mmol), and benzoyl peroxide (0.28 g, 1.2 mmol) was heated at 80° C

Component	High Mass Peak	Adduct Assignment
l (minor)	233	1:1 M-H
2 (major)	234	1:1 M
3 (major)	234	1:1 M
4 (major)	234	1:1 M
5 (minor)	278	2:1 M-C ₂ H ₄
6 (minor)	263	2:1 $M - C_3 H_7$
7 (minor)	235	2:1 M-C ₃ H ₇ CO

for 17 h. A liquid (9.0 g) and (1) (4.1 g) were recovered. The liquid was shown to contain the following by m.s.-g.l.c.:

The mixture was distilled to give a liquid (4.0 g), b.p. $80-90^{\circ}C$ at 0.5 mm Hg, which contained only the three major components. One of these was isolated by preparative scale g.l.c. and identified as (E)-3-trifluoro-methyl-1,l,l-trifluorohept-2-en-4-one (16) (nc): Analysis: C, 41.1; H, 3.3; F, 49.0%; M⁺, 234. $C_8H_8F_60$ requires: C, 41.03; H, 3.42; F, 48.72%; M, 234; ν_{max} (C=0) 1725 cm⁻¹; δ_F 62.7 (3F, dq, J 7.5 and 1.5 Hz, F_a) and 67.0 (3F, broad, F_b); δ_H 0.95 (3H, t, J 7 Hz, CH₃), 1.71 (2H, sx, J 7 Hz, CH₃-), 2.72 (2H, t, J 7 Hz, C₂H₅CH₂-), and 6.42 (1H, qq, J 7.5 and 1.3 Hz, CH).

A complex mixture of products was also obtained when the reaction was repeated using gamma-ray initiation.



(16)

Reaction of (1) with alcohols

(a) Methanol (with N. Kelly)

A mixture containing hexafluoro-2-butyne (1) (17.0 g, 105 mmol) and methanol (12.18 g, 380 mmol) was irradiated to a dose of 5.4 x 10^6 rad. Compound (1) (2.42 g) was recovered and a liquid (23.84 g) was obtained. Transference under vacuum from the liquid gave mainly trans-2-methoxy-3H-heptafluorobut-2-ene (7) (12.82 g), by comparison of its spectroscopic data [9]. The residual liquid (10.52 g) was washed with water, the lower layer separated, dried (MgSO₄) to give, by preparative scale g.l.c. (column 0, 115° C), (E)-(2-trifluoromethyl)-4,4,4-trifluorobut-2-en-1-ol (8) (nc) (2.4 g, 12%): b.p. 104°C; Analysis: C, 30.7; H, 2.3; F, 58.3%; M⁺, 194. C₅H₄F₆O requires: C, 30.92; H, 2.06; F, 58.76%; M, 194; $\delta_{\rm F}$ 60.4 (3F, d, J 8 Hz, F_a) and 69.2 (3F, t, J 2 Hz, F_b); $\delta_{\rm H}$ 4.32 (1H, broad, s, OH), 4.53 (2H, s, CH₂), and 6.42 (1H, q, J 8 Hz, CH).



(b) 2,2,2-Trifluoroethanol

A mixture containing 2,2,2-trifluoroethanol (9.6 g, 96 mmol) and hexafluoro-2-butyne (1) (5.4 g, 33 mmol) was irradiated to a dose of 1.6 x 10⁷ rad. Compound (1) (4.0 g) was recovered and 2,2,2-trifluoroethanol was partially removed by distillation to leave a liquid (2.1 g), which was shown by g.l.c. to contain the alcohol and three other components. Separation by preparative scale g.l.c. gave (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (9) (nc) (0.5 g, 22%): Analysis: C, 27.2; H, 1.1; F, 65.4%; M, 223 (M⁺-39). C₆H₂F₀O requires: C, 27.48; H, 1.15; F, 65.27%; M, 262; $\delta_{\rm F}$ 61.5 (3F, broad, $F_{\rm a}$), 64.9 (3F, d, J 7.8 Hz, $F_{\rm b}$), and 77.6 (3F, broad, F_{c}); δ_{H} 3.80 (1H, s, OH), 5.15 (1H, q, J 6.4 Hz, > CH), and 6.30 (1H, q, J 7.8 Hz, -CH=); and (Z)-3-trifluoromethyl-1,1,1,5,5,5hexafluoropent-2-en-4-ol (10) (nc) (0.5 g, 22%); Analysis: C, 27.3; H, 1.1; F, 65.3%; M, 223 (M⁺-39). C₆H₂F₉O requires: C, 27.48; H, 1.15; F, 65.4%; M, 262; δ_{F} 61.5 (3F, q, J 10 Hz, F_{a}), 62.7 (3F, complex m, F_{b}), and 80.0 (3F, broad, F_{c}); δ_{H} 3.10 (1H, d, J 5 Hz, OH), 4.63 (1H, broad m,>CH), and 6.42 (1H, q, J 8 Hz, -CH=).



Reaction of (1) with ditertiarybutyl peroxide

A mixture containing hexafluoro-2-butyne (1) (1.7 g, 10 mmol) and di-tertiarybutyl peroxide (0.1 g, 0.7 mmol) was heated at $132^{\circ}C$ for 18 h.

The yellow liquid (0.4 g), which was obtained, was found to contain nine components by g.l.c. (column A) and the high mass peaks of the major components are as follows: (i) 178, $CH_3-(CF_3)=CHCF_3$; (ii) 340, $CH_3-[C(CF_3)=C(CF_3)]_2-H$; (iii) 58, CH_3COCH_3 ; (iv) 340, isomer of ii; (v) 502, $CH_3-[C(CF_3)=C(CF_3)]_3-H$; and (vi) 664, $CH_3-[C(CF_3)=C(CF_3)]_4-H$.

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