Journal of Fluorine Chemistry, 22 (1983) 123–132

Received: June 17, 1982

POLYFLUOROBICYCLO(2,2,1)HEPTANES. PART XII. 4H-DECAFLUOROBICYCLO(2,2,1)HEPT-1-YL ISOCYANATE, AMINE AND ALCOHOL, AND DERIVATIVES THEREFROM *

JOHN S. BROUGHTON, PETER LYNCH, ROBERT STEPHENS and JOHN COLIN TATLOW

Chemistry Department, The University of Birmingham, P.O. Box 363, Birmingham, B15 2TT (U.K.)

SUMMARY

4H-Decafluorobicyclo(2,2,1)hept-1-yl carboxylic acid chloride gave the corresponding isocyanate which readily afforded appropriate derivatives of carbamic acid, and substituted ureas, all with the bridgehead moiety substituted on nitrogen. The 4H-bridgehead primary amine was made from the isocyanate and directly from the acid chloride. Diazotisation converted it mainly to the bridgehead tertiary alcohol, with traces of the derived nitrite ester, and of the bridgehead chloride and dihydro-compound. Peroxidic oxidation of the amine gave the bridgehead nitro-compound.

INTRODUCTION

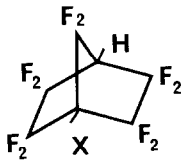
We have done much synthetic work on polyfluoro-bicyclic systems, particularly norbornanes [1] and bicyclo-octanes [2]. The hydrogen at the bridgehead positions in the precursors is not readily removed on fluorination, and polyfluoro-compounds with bridgehead hydrogen are valuable synthetic intermediates in both series. In basic media, they react as bridgehead carbanions with many nucleophile acceptors; ranges of compounds have been made with functional groups on bridgehead positions. This paper describes some compounds with bridgehead substituents, particularly $-NH_2$ and -OH, less easy to insert by the above approach, and which have been made therefore by classical synthetic procedures.

* Presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland, Sept. 1974.

0022-1139/83/0000-0000/$03.00

RESULTS

The starting point for the present syntheses was 1H,4H-decafluorobicyclo(2,2,1)heptane* [3] (1; see Scheme), which by metallation followed by carbonation had afforded, in earlier work [4], 4H-decafluorobicyclo-(2,2,1)hept-1-yl carboxylic acid (2). We found that yields were improved to 65% if the metallation of 1 was done with butyl lithium [cf. 5]. With phosphorus pentachloride this acid (2) gave its acid chloride (2a), which was converted in the normal way to the β-naphthyl ester (2b) and anilide (2c).



1 X = H
3 X = N=C=O
4 X = NH_2
7 X = Cl
8 X = OH
8a X = O-N=O
8b X = $O-COC_6H_5$
9 X = NO_2

2 X= COOH
2a X= $C(=O)-Cl$
2b X= $C(=O)-O-C_{10}H_7$-2
2c X= $C(=O)-NHC_6H_5$

5a X= $NH\cdot C(=O)\cdot O\cdot C_{10}H_7$-2
5b X= $NH\cdot C(=O)\cdot O\cdot n$-Pr
5c X= $NH\cdot C(=O)\cdot O\cdot CH_2C_7F_{11}$-1
6a X= $NH\cdot C(=O)\cdot NH\cdot C_6H_5$
6b X= $NH\cdot C(=O)\cdot NH\cdot C_7F_{10}H$-1,4

SCHEME

On a practical note, all the compounds made, except the isocyanate (3), were solids, following the usual pattern for polyfluorobicyclo(2,2,1)-heptanes. All the melting point determinations were done in sealed tubes,

*Caution: this compound has powerful anaesthetic activity and may be toxic.

since many of the compounds were quite volatile, particularly at temperatures near their melting points. Structures of compounds were clear from analytical data and the synthetic procedures used. The appropriate ir bands were found in the spectra, and the standard ^{19}F nmr pattern for these compounds was always present, showing that no rearrangements had occurred. In the ^{1}H nmr spectra, there was always a broad absorption, in the region 5-6.5 τ, for the bridgehead hydrogen at position 4, together with other appropriate bands.

The acid chloride (2a) reacted readily with aqueous sodium azide in a standard Curtius rearrangement, though a mixed product was obtained. After prolonged hydrolysis with concentrated potash this mixture afforded the desired bridgehead primary amine (4). Perhaps surprisingly, the yields in the best reactions were quite good, but the process was troublesome, and an alternative approach was sought. The reported [6] conversion of perfluoro-n-alkane carboxylic acid chlorides to isocyanates, using trimethylsilyl azide, was applied to the acid chloride (2a). Reaction was sluggish, but the required isocyanate (3) was obtained without difficulty, though only in moderate yield.

Isocyanate 3 was highly reactive towards nucleophiles, and reacted quickly with water to give a mixture of products. Careful addition of 3 to diethyl ether saturated with water gave an almost quantitative conversion to the bridgehead amine (4). With β-naphthol, propan-1-ol, and undecafluorobicyclo(2,2,1)hept-1-ylmethanol [7], the isocyanate (3) reacted quickly, to give good yields of the appropriate N-(4H-decafluorobicyclo-(2,2,1)hept-1-yl) carbamates (5a, 5b, 5c, respectively). The ready reaction, to give 5c, with the relatively acidic bridgehead-substituted methanol, a poor nucleophile, is noteworthy.

With aniline, the isocyanate (3) gave a di-substituted urea (6a). Also, it reacted quite readily with the bridgehead primary amine (4), to give a good yield of the symmetrical urea (6b). This had been one of the constituents of the product mixture obtained when the isocyanate was treated with water and explained the problems with that reaction. Again, the isocyanate (3) is capable of reacting with a very weakly nucleophilic fluorinated species.

The bridgehead amine (4) reacted smoothly with sodium nitrite/hydrochloric acid, and, after a short reflux period, work-up gave a little recovered amine (4), and three minor and one major product. The last was the desired bridgehead tertiary alcohol (8) (yield 55%). The minor products

were the bridghead dihydro-compound (1) (7%), the 1H-4-chloride (7) (<1%), and 8% of the nitrite ester (8a) of the alcohol 8. Repitition of the experiment using a greater excess of hydrochloric acid gave: 1 (2.6%); 7 (7%); 8(a) (4.5%); and 8 (60%); with no unreacted 4 detected.

The usually-accepted diazotisation pathway [8], involving an intermediate behaving as a carbonium ion, could explain this result. The fragments incorporated to give products 8, 8a, and 7 were all present as parts of species sufficiently nucleophilic to react with such an intermediate. However, the formation of the dihydro-compound (1) is less easy to explain. Further, at bridgehead positions, carbonium ions are not thought to form readily [9], even less so presumably in this electronegatively-substituted series. It is possible therefore that in this diazotisation there is a free-radical pathway competitive with the ionic one.

Alcohol 8 did not react with 2,4-di-nitrochlorobenzene, but with benzoyl chloride gave a good yield of its benzoate ester (8b). Nitrosyl chloride converted it to the nitrite ester (8a), but sluggishly, and in poor yield.

Oxidation of the amine 3 was done with $H_2O_2/(CF_3CO)_2O$ to give a low yield of the bridgehead nitro-compound (9), with much recovered amine. Reaction with $H_2O_2/H{\cdot}CO_2H$ gave a deep blue colour, but no nitroso-compound could be identified, and, after a very prolonged sequence, only the nitro-compound (9) was isolated.

The amine (4) is an example of an interesting type of compound, having a primary amino group carried on a tertiary carbon (i.e. itself carrying no fluorines) within a fluorocarbon moiety. The work-up from the first method of synthesis, via the Curtius rearrangement, showed the high stability of this particular example (4). It had little basic character, and did not react with 2,4-dinitrochlorobenzene.

A primary amine of this general type, but arising by direct amination of a substituted cyclobutene, derived ultimately from the major hexamer of tetrafluoroethylene, has been made in our group [10], whilst Knunyants and co-workers [11] have reported tris(trifluoromethyl)methylamine, made by reduction of the nitroso-compound. This amine was made also [12] by hydrolysis of tris(trifluoromethyl)methyl isocyanate, which was not specially reactive, and did not give a symmetrical urea with tris(trifluoromethyl)methylamine [12]. Reactions of amines of this type with nitrous acid are of considerable interest, though not often reported. In

the case of the amino-cyclobutene above [8], a fluorocarbon alcohol was obtained, but the OH was on a different carbon than that bearing the original NH_2, owing to an allylic rearrangement involving a double bond adjacent to the amino-centre. Tris(trifluoromethyl)methylamine gave a roughly 2:1 mixture of the corresponding alcohol and nitroso-compound. Amine 4 gives alcohol 8 in reasonable yield from a smooth reaction.

EXPERIMENTAL

Gas liquid chromatography Semi-preparative work was done in glass columns (9.1 m x 8 mm internal diameter) in Pye series 104 or 105 instruments. Columns were packed using 30-60 mesh Chromasorb as solid support: column A with di-isodecyl phthalate (1:3); column B with polyethylene glycol adipate (1:5); and column C with Carbowax 6000 (1:4). Similar packings were used for analytical work. Column temperature and nitrogen flow rate (ℓ/h^{-1}) are given for each separation.

Spectroscopy Infrared spectra (ir) was recorded on a Perkin-Elmer PE 257 machine: measurements in Nujol mulls are marked N; liquid films, L; and vapour phase, V: band positions are cm^{-1}. Nuclear magnetic resonance (nmr) spectra were measured in solutions in carbon tetrachloride, deuterochloroform, or hexadeuteroacetone, on a Perkin-Elmer R 10 instrument; ^1H at 60 MHz (τ units; tetramethyl silane as internal reference: s = singlet, t = triplet, b = broad, cm = complex multiplet); ^{19}F at 56.4 MHz (trichlorofluoromethane as internal reference). In all cases the ^{19}F spectra showed the characteristic pattern of AB quartets typical of decafluorobicyclo(2,2,1)heptanes, and details are not recorded.

Derivatives of 4H-decafluorobicyclo(2,2,1)heptane-1-carbonyl chloride (2a) (a) The acid chloride [1; m.p. 53-54°] (1.00 g), β-naphthol (0.43 g), dry benzene (10 cm^3), and pyridine (0.5 cm^3; dried over KOH and distilled) were refluxed together for 3 h. Solvent was removed on a rotary evaporator, and the residue recrystallised from light petroleum (b.p. 60-80°) to give β-naphthyl 4H-decafluorobicyclo(2,2,1)-heptane-1-carboxylate (2b) nc (0.70 g), m.p. 139-141° (Found: C, 48.3; H, 1.8; F, 42.2. $C_{18}H_8F_{10}O_2$ requires C, 48.4; H, 1.8; F, 42.6%); ir (N) 1780 (s) (C=O); ^1H nmr 6.4 (b), cm centred at 2.4, relative intensity 1:7.

(b) Freshly distilled aniline (1 cm^3) was added dropwise to acid chloride (2a) (1.5 g) in dry benzene (10 cm^3). A precipitate of aniline hydro-

chloride was filtered off, and the filtrate and washings then worked up as above, to give the N-phenyl amide of 4H-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (2c) nc (1.1 g) m.p. 103-104° (Found: C, 42.8; H, 1.9; F, 47.8; N, 3.5. $C_{14}H_7F_{10}NO$ requires C, 42.55; H, 1.8; F, 48.1; N, 3.5%); ir (N) 3320 (m), 1525 (s) (NH), 1700 (s) (C=O); ^{1}H nmr 6.3 (b), cm centred at 2.6, relative intensity 1:6.

1-Isocyanato-4H-decafluorobicyclo(2,2,1)heptane (3) Trimethylsilyl azide (6.5 g) was added dropwise to the acid chloride (2a) (18.9 g) in an atmosphere of nitrogen. The mixture was stirred mechanically at 100° for 24 h. Fractional distillation through a 1' column packed with glass helices gave:- (i), a mixture (7.0 g), b.p. 57-100°, shown by glc to be mainly trimethylsilyl chloride and trimethylsilyl azide containing ca 10% of polyfluoro-material: (ii), a mixture (14.2 g), b.p. >100°. Separation of fraction (ii) by glc (A, 130°, 5) gave (ii)a, 1-isocyanato-4H-decafluorobicyclo(2,2,1)heptane (3) nc (5.0 g), b.p. 134-135° (Found: C, 30.0; H, 0.5; F, 59.7; N, 4.7. $C_8HF_{10}NO$ requires C, 30.3; H, 0.3; F, 59.9; N, 4.4%); ir (L) 2280 (vs) (N=C=O), 1790 (s) (C=O), 1500 (m) (N=C), 3020 (w) (CH); ^{1}H nmr, 6.4 (b) : (ii)b, acid chloride (2a) (7.5 g) (correct ir).

1-Amino-4H-decafluorobicyclo(2,2,1)heptane (4)

(a) From the acid chloride (2a) Compound 2a (5.0 g) was added to a well-stirred solution of sodium azide (2.0 g) in water (20 cm^3), which was then refluxed for 4 h. Extraction with ether, followed by its evaporation, left a residue (3.8 g) which was refluxed for 8 h with aqueous potassium hydroxide (10 cm^3; 50% w/w). Extraction with ether, followed by its evaporation, left the crude product, which was sublimed at 14 mm pressure to give 1-amino-4H-decafluorobicyclo(2,2,1)heptane (4) nc (3.1 g), m.p. 155-157° (Found: C, 28.8; H, 1.1; F, 65.9; N, 4.7. $C_7H_3F_{10}N$ requires C, 28.9; H, 1.0; F, 65.3; N, 4.8%); ir (N) 3440 and 3360 (m), 1625 (m) (NH).

(b) From the isocyanate (3) Compound 3 (10.0 g) was added dropwise to a well-stirred saturated solution of water in diethyl ether (40 cm^3), a gas being evolved: stirring was maintained for 15 h. The solution was dried ($MgSO_4$), the ether distilled off through a short fractionating column, and the residue purified as above, to give the amine (4) (9.0 g), with a correct ir spectrum.

Carbamates from the isocyanate (3) (a) Isocyanate 3 (1.0 g) was added dropwise to β-naphthol (0.45 g) in dry benzene (5 cm^3). The solution was

refluxed for 45 min, and the benzene then removed using a rotary evaporator. Recrystallisation of the residue from a 1:1 mixture of chloroform and light petroleum (b.p. 80-100°) gave β-naphthyl N-[4H-decafluorobicyclo(2,2,1)hept-1-yl]carbamate (5a) nc (0.9 g), m.p. 149-150° (Found: C, 47.1; H, 2.0; F, 41.1; N, 3.1. $C_{18}H_9F_{10}NO_2$ requires C, 46.9; H, 2.0; F, 41.2; N, 3.0%); ir (N) 3300 (m) 1535 m (NH), 1735 (s) (C=O); ^{1}H nmr, 5.2 (b), cm centred at 2.4, 1.2 (s), in the ratio 1:7:1.

(b) Isocyanate 3 (0.53 g) was added dropwise to propan-1-ol (0.1 g) in dry ether (5 cm^3). After 15 h at 15°, the solvent was evaporated off, and the residue sublimed at 14 mm pressure, to give prop-1-yl N-[4H-decafluorobicyclo(2,2,1)hept-1-yl]carbamate (5b) nc (0.56 g), m.p. 115-116° (Found: C, 35.4; H, 2.5, F, 50.3; N, 3.8. $C_{11}H_9F_{10}NO_2$ requires C, 35.0; H, 2.4; F, 50.4; N, 3.7%); ir (N) 3280 (s) 1550 (s) (NH), 1720 (s) (C=O); ^{1}H nmr, 9.1 (t, J=7.5), 8.3 (sextet, J=6.0), 6.0 (t, J=6.0), 5.5 (b), 2.2 (s), in intensity ratio 3:2:2:1:1.

(c) Isocyanate 3 (0.5 g) was added dropwise to undecafluorobicyclo(2,2,1)-hept-1-yl methanol [7] (0.5 g) in dry ether (20 cm^3). After refluxing for 1 h, evaporation of the solvent left a residue: recrystallisation from light petroleum (b.p. 100-120°) gave undecafluorobicyclo(2,2,1)hept-1-yl-methyl N-[4'H-decafluorobicyclo(2,2,1)hept-1'-yl]carbamate (5c) nc (0.7 g), m.p. 190-191° (Found: C, 29.7; H, 0.5. $C_{16}H_4F_{21}NO_2$ requires C, 30.0; H, 0.6%; ir (N) 3280 (m) (NH), 1740 (s) (C=O); ^{1}H nmr, 5.4 (b), 5.6 (c), 5.0 (c), 1.0 (s), ratio 1:1:1:1.

Substituted ureas from the isocyanate (3)

(a) Isocyanate (0.8 g) added dropwise to aniline (0.25 g) in dry ether (5 cm^3), gave an immediate precipitate. Ether was evaporated off and the residue recrystallised from chloroform/ethanol (3:2) to give N-[4H-decafluorobicyclo(2,2,1)hept-1-yl] N'-phenyl urea (6a) nc (1.0 g), m.p. 272-274° (Found: C, 41.0; H, 2.2; F, 45.8; N, 6.7. $C_{14}H_8F_{10}N_2O$ requires C, 41.0; H, 2.0; F, 46.3; N, 6.8%); ir (N) 3380 and 3330 (s) (NH), 1670 (s) (C=O); ^{1}H nmr 5.4 (b), 2.9 (cm), 1.9 (s), relative ratio 1:6:1.

(b) Isocyanate 3 (0.20g) was added dropwise to amine 4 (0.19 g), in dry benzene (5 cm^3). After being refluxed for 4 h, the solvent was evaporated off, and the residue was recrystallised from light petroleum (b.p. 80-100°) to give N,N'-bis[4H-decafluorobicyclo(2,2,1)hept-1-yl]urea (6b) nc (0.35 g), m.p. 322-323° (Found: C, 29.5; H, 1.0; F, 62.5; N, 4.8. $C_{15}H_4F_{20}N_2O$ requires C, 29.6; H, 0.7; F, 62.5; N, 4.6%); ir (N) 3360 (s) 1570 (s) (NH), 1710 (s) (C=O); ^{1}H nmr 5.3 (b), 2.6 (s), ratio 1:1.

Diazotization of the amine (4) A solution of sodium nitrite (2.13 g) in water (10 cm^3) was added dropwise to a well-stirred suspension of the amine (4) (3.0 g) in hydrochloric acid (26 cm^3; 4 M) at 0°. After $^1/_2$ h further at 0°, the mixture was refluxed for 2 h, and was then cooled and extracted several times with ether. The combined extracts were dried ($MgSO_4$), filtered, and the bulk of the ether distilled off through a short column. Separation of the residue by glc (B, 150°, 5) gave three fractions, (i) (ii) and (iii).

Fraction (i) was a mixture, separated by further glc (C, 120°, 5) to give (ether not collected):- (i)a, 1-chloro-4H-decafluorobicyclo(2,2,1)-heptane (7) (0.02 g) [1]: (i)b, 1H,4H-decafluorobicyclo(2,2,1)heptane (1) (0.20 g) [3,4]: (i)c, 4H-decafluorobicyclo(2,2,1)heptan-1-yl nitrite (8a) nc (0.25 g), m.p. 144-145° (Found: C, 26.0; H, 0.5; F, 58.7; N, 4.5. $C_7HF_{10}NO_2$ requires C, 26.2; H, 0.3; F, 59.2; N, 4.4%); ir (V) 1590 (s) (N=O); ^{1}H nmr, 6.3 (b).

Fraction (ii) was recovered amine (4) (0.1 g).

Fraction (iii) was 4H-decafluorobicyclo(2,2,1)heptan-1-ol (8) nc (1.6 g), m.p. 109-111° (Found: C, 28.6; H, 1.0; F, 64.9. $C_7H_2F_{10}O$ requires C, 28.8; H, 0.7; F, 65.0%); ir (N) 3200-3600, 1615 (w) (OH); ^{1}H nmr, 5.5 (b), 1.7 (vb).

Compounds (i)a, (i)b, and (ii) were identified by glc and ir.

Sodium nitrite solution as above was added to the amine (4) (2.0 g) in hydrochloric acid (20 cm^3; 4 M). After $^1/_2$ h at 0°, concentrated hydrochloric acid (30 cm^3) was added, and the mixture was refluxed for 2 h. Isolation as above gave:- (i)a, the chloride (7) (0.15 g), m.p. 108-109°: (i)b, the dihydro-compound (1) (0.05 g): (i)c, the nitrite (8a) (0.1 g): (ii), the alcohol (8) (1.2 g): all were identified by ir.

Esters from the alcohol (8)

(a) Butyl lithium (2.5 cm^3; 2.1 M in hexane) was added dropwise to well-stirred alcohol (8) (0.75 g) in dry ether (20 cm^3) at -60°. After 30 min., nitrosyl chloride was bubbled into the solution for 5 min. and stirring continued for 2 h further at -60°. The solution was allowed to warm to room temperature, and was distilled in vacuo to remove the fluorocarbon material. Glc separation (B, 120°, 5) gave (i), ether and hexane: (ii), 4H-decafluorobicyclo(2,2,1)hept-1-yl nitrite (8a) (0.05 g): (iii), recovered alcohol (8) (0.3 g): all were identified by ir.

(b) The alcohol (0.2 g), benzoyl chloride (0.09 g), dry benzene (5 cm^3) and a few drops of pyridine were refluxed together for 4 h. Solvent was evaporated off, the residue taken up in ether, washed with dilute hydrochloric acid, and water, and dried ($MgSO_4$). After removal of ether, the residue was sublimed (80°/14 mm pressure) to give 4H-decafluorobicyclo(2,2,1)hept-1-yl benzoate (8b) nc (0.25 g), m.p. 101-102° (Found: C, 42.2; H, 1.8; F, 47.8. $C_{14}H_6F_{10}O_2$ requires C, 42.4; H, 1.5; F, 48.0%); ir (N) 1760 (s) (C=O).

Oxidation of the amine (4)

(a) A solution of 4 (3.3 g) in dichloromethane (6 cm^3) was added dropwise to a well-stirred refluxing mixture of hydrogen peroxide (2 cm^3; 90%) trifluoroacetic anhydride (5 cm^3) and dichloromethane (20 cm^3): a blue colouration developed. After 1 h, hydrogen peroxide (1 cm^3; 90%) was added (yellow colouration) and refluxing was then continued for 20 h further. The mixture was then cooled, washed with water, dried ($MgSO_4$) and the solvent distilled off through a short column. The residue was sublimed at 14 mm pressure to give a mixture (2.2 g). Glc separation (C, 120°, 5) gave:- (i), 1-nitro-4H-decafluorobicyclo(2,2,1)heptane (9) nc (0.35 g), m.p. 142-143° (Found: C, 26.1; H, 0.5; F, 58.9; N, 4.3%); ir (N) 1580 (s) (N=O); ^1H nmr, 6.3 (b): (ii), recovered amine (4) (1.2 g), with a correct ir spectrum.

(b) Amine 4 (4.2 g) in dichloromethane (25 cm^3) was added dropwise to a well-stirred refluxing mixture of formic acid (25 cm^3; 90%), hydrogen peroxide (10 cm^3; 90%) and dichloromethane (100 cm^3). A blue colour developed. After 24 h, the organic layer was separated off and fresh peroxide and formic acid added, and refluxing then continued. This was done six times in all over a total period of one week. Working up as for (a) afforded the nitro-compound (9) (3.2 g) (correct ir).

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