*Journal of Fluorine Chemistry*, 20 (1982) 167–171

Received: June 10, 1981

# FLUOROCYCLOHEXANES PART XV [1] DEHYDROFLUORINATIONS OF UNDECA- DECA- AND NONA- FLUOROCYCLOHEXANES

PAUL L. COE, ANDREW W. MOTT AND JOHN COLIN TATLOW

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

## SUMMARY

An experimental modification has improved dehydrofluorinations of undeca- deca- and nona- fluorocyclohexanes, and enhanced the proportions of dienes and aromatics formed.

## INTRODUCTION

In general organic chemistry, base-promoted dehydrohalogenations are usually conducted in homogeneous media, using bases or alkoxides dissolved in alcohols. In most cases the olefinic product is not particularly susceptible to nucleophilic attack. In fluorocarbon chemistry this is not so, fluorocarbon olefins will react readily with the base used if generated in a homogeneous medium. In our early work on fluorocyclohexanes (see literature cited in Table 1) we found that heterogeneous dehydrofluorinations, carried out by refluxing with aqueous potassium hydroxide proceeded fairly readily as far as the production of unsaturates. Fortunately for the progress of the work, although these products were destroyed in time if exposed to hot aqueous alkali, such reactions went very much more slowly than the dehydrofluorinations. In nearly all cases therefore, with suitable choice of reaction conditions, and despite long reflux times, reasonably good yields of fluorocyclohex-enes and -dienes could be obtained. Further, using nona- and octa- fluorocyclohexanes as starting materials, hexa- and penta- fluorobenzene, respectively, were formed as well, the start of our aromatic fluorocarbon work [6].

0022-1139/82/0000-0000/$02.75

Recently we required quantities of various fluorocyclohex-enes and -dienes as starting materials for epoxidation reactions [7]. In making these precursors an improvement was found for our general heterogeneous dehydrofluorination process, and this is now described.

## RESULTS

Polyfluorocyclohexanes were dehydrofluorinated with aqueous potassium hydroxide as before, but using a vibro-stirrer and surfactant to intimately mix the refluxing phases, and employing less concentrated alkali solutions than hitherto.

Much shorter reaction times were needed, 15 - 30 mins instead of many hours.

The products were the same as those isolated from the earlier reactions but the proportions differed. There were usually greater amounts of dienes and aromatics (see Table 1). In most cases, overall recoveries were improved and certainly yields of products with maximum unsaturation were better. Under these conditions dehydrofluorination of the mixed 1H/3H- and 1H/4H- decafluorocyclohexanes gave entirely perfluorocyclohexadienes with more of the 1,3-isomer isolated. Under old conditions, mono-enes were left and there had clearly been some decomposition of the $C_6F_8$-1,3.

1H,4H/2H-Nonafluorocyclohexane gave more hexafluorobenzene than hitherto after 15 min under reflux, but also reacted at room temperature, all starting material being consumed in 3 hours or so. Even refluxing potassium carbonate solution effected 37% dehydrofluorination to 3H/4H-octafluorocyclohexene; an interesting selectivity effect. It is clear that if mono-olefins are required quite mild conditions would suffice for their production, probably in good yield with little ongoing dehydrofluorination. The primary dehydrofluorination products from 1H, 4H/2H-nonafluorocyclohexane, 3H/4H- and 4H/5H-octafluorocyclohex-1-ene, were found in the present series of reactions in smaller proportions than from our previous experiments, and there was much less of the latter than the former. Clearly, the 3H/4H-ene is more resistant to further dehydrofluorination than is the 4H/5H-ene, a fact not realised before.

TABLE 1.

Dehydrofluorinations of Polyfluorocyclohexanes

| Starting Material | | | | Alkali | | Re-action Time (mins) | Products | | |
|---|---|---|---|---|---|---|---|---|---|
| Literature Ref. | Structure | B.p. (°C) | Wgt. (g) | KOH (g) | $H_2O$ (cm³) | | Total Yield (g) | Structure | Weight (g) |
| 2 | $C_6HF_{11}$ | 63 | 50 | 50 | 150 | 30 | 38 | $C_6F_{10}$ | 38 |
| 3 | $C_6H_2F_{10}$ | 78 | 50 | 50 | 150 | 45 | 33 | $C_6F_8$-1,4 | 10.6 |
| | 1H/3H | | | | | | | $C_6F_8$-1,3 | 21.4 |
| | +1H/4H | | | | | | | | |
| 4 | $C_6H_3F_9$ | 93 | 20 | 20 | 60 | 15 | 12 | $C_6HF_7$-3 isomers | 5.1 |
| | 1H,4H/2H | | | | | | | $C_6F_6$ | 2.8 |
| | | | | | | | | $C_6H_2F_8$-3H/4H | 3.0 |
| | | | | | | | | $C_6H_2F_8$-4H/5H | 0.2 |
| 4 | $C_6H_3F_9$ | 101 | 25 | 25 | 75 | 15 | 15 | $C_6HF_7$-3 isomers | 6.8 |
| | 1H/2H,4H | | | | | | | $C_6F_6$ | 3.6 |
| | | | | | | | | $C_6H_2F_8$-3H/4H | 4.0 |
| | | | | | | | | $C_6H_2F_8$-4H/5H | 0.2 |
| 5 | $C_6H_4F_8$ | 118 | 25 | 25 | 75 | 15 | 15 | $C_6H_2F_6$-2 isomers | 0.3 |
| | 1H,4H/2H,5H | | | | | | | $C_6HF_5$ | 5.8 |
| | | | | | | | | $C_6H_3F_7$-1H,4H/5H | 8.8 |
| | " | " | " | 75 | " | " | 13 | " | 1.5 |
| | | | | | | | | " | 7.7 |
| | | | | | | | | " | 2.9 |
| 5 | $C_6H_4F_8$ | 125 | 25 | 25 | 75 | 15 | 16 | $C_6H_2F_6$-2 isomers | 2.5 |
| | 1H,5H/2H,4H | | | | | | | $C_6HF_5$ | 8.0 |
| | | | | | | | | $C_6H_3F_7$-1H,4H/5H | 5.1 |
| 5 | $C_6H_4F_8$ | 133 | 15 | 17 | 50 | 15 | 13 | $C_6H_2F_6$-2 isomers | 9.3 |
| | 1H,2H/4H,5H | | | | | | | $C_6HF_5$ | 2.4 |
| | | | | | | | | $C_6H_3F_7$-1H,4H,5H/ | 0.4 |
| 5 | $C_6H_4F_8$ | 136 | 8 | 10 | 30 | 15 | 7 | $C_6H_2F_6$-2 isomers | 1.2 |
| | 1H,2H,4H/5H | | | | | | | $C_6HF_5$ | 1.1 |
| | | | | | | | | $C_6H_3F_7$-1H,4H/5H | 4.5 |
| | " | " | " | " | " | 30 | 4 | " | 0.7 |
| | | | | | | | | " | 1.0 |
| | | | | | | | | " | 2.0 |

It is clear from vibro-stirred reactions carried out for longer times that dienes and aromatics are also attacked more readily by potassium hydroxide under these conditions. Reactions must therefore not be carried on for too long. Dehydrofluorinations by strong bases must always be a delicate compromise chosen to give maximum loss of hydrogen fluoride from the starting material, but without significant nucleophilic attack on the unsaturated products.

This type of heterogeneous dehydrohalogenation could be of wide utility in organic chemistry.

## EXPERIMENTAL

Dehydrofluorination was carried out in a Pyrex flask fitted with a water cooled double surface condenser above a simple condenser. The size of flask was always at least three times the combined volumes of fluorocarbon and aqueous potassium hydroxide used.

Stirring was carried out using a Chemi-Apparatebau vibrating stirrer fitted with a 40 mm diameter brass paddle into which were drilled 8 5mm diameter holes.

An antifoaming agent was necessary (Fisons Silicone antifoam was used).

All analytical glc was carried out using glass tubing 1.8m x 4mm internal diameter packed with dinonyl phthalate/celite (1:5) fitted in a Pye series 104 instrument ($80^o$, $N_2$ 2 $lh^{-1}$). Preparative glc was done in a copper tube 4.8m x 35mm internal diameter packed with dinonyl phthalate on Chromosorb P 30-60 (1:5) and using a Katharometer detector ($85^o$, $N_2$ 10 $lh^{-1}$).

### General method as illustrated by the dehydrofluorination of mixed 1H/3H and 1H/4H-decafluorocyclohexanes (b.p. $78^o$)

Decafluorocyclohexane (50g), potassium hydroxide (50g), water (150 $cm^3$) and silicone antifoam agent (0.5 $cm^3$) were refluxed with vibro-stirring for 45 minutes. The mixture was allowed to cool, diluted with water (300 $cm^3$), and the organic layer was separated, washed and dried ($MgSO_4$). The product (33.1g) contained two components which were separated by preparative glc to yield i) octafluorocyclohexa-1,4-diene (10.6g); ii) octafluorocyclohexa-1.3-diene (21.4g); with correct i.r. spectra.

Details of reactions carried out are given in Table 1.

Other Dehydrofluorinations of 1H, 4H/2H- Nonafluorocyclohexane

The compound (20g) KOH (30g) and water (90 $cm^3$) with antifoaming agent (0.5 $cm^3$) were vibro-stirred at room temperature (ca $15^0$). Samples were analysed by glc as follows, (percentages calculated from peak areas).

| Time (h) | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
|---|---|---|---|---|---|---|---|---|---|
| $C_6H_3F_9$ | 92 | 84 | 38 | 25 | 5 | 1 | - | - | - |
| $C_6H_2F_8$-2 isomers | 4 | 8 | 34 | 30 | 32 | 26 | 24 | 23 | 23 |
| $C_6F_6$ | - | - | 3 | 8 | 20 | 20 | 21 | 26 | 20 |
| $C_6HF_7$ -3 isomers | 4 | 8 | 23 | 37 | 43 | 53 | 53 | 51 | 57 |

The compound (10g) potassium carbonate (40g) water (40 $cm^3$) and antifoaming agent (0.5 $cm^3$) were refluxed and vibro-stirred for 3h. Glc analysis showed the presence of starting material (63%) and 3H/4H-octafluorocyclohexene (37%).

## REFERENCES

1 Part XIV, P.L. Coe, J.H. Sleigh and J.C. Tatlow, J. Fluorine Chem., 15 (1980) 339.

2 J.C. Tatlow and R.E. Worthington, J. Chem. Soc., (1952) 1251.

3 D.E.M. Evans and J.C. Tatlow, ibid., (1954) 3779: (1955) 1184: D.E.M. Evans, J.A. Godsell, R. Stephens, J.C. Tatlow and E.H. Wiseman, Tetrahedron, 2 (1958) 183.

4 J.A. Godsell, M. Stacey, and J.C. Tatlow, ibid., p. 193.

5 E. Nield, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1959) 159.

6 J.C. Tatlow, Endeavour, 22 (1963) 89.

7 P.L. Coe, A.W.Mott, and J.C. Tatlow, J. Fluorine Chem., (in the press)