*Journal of Fluorine Chemistry, 28* (1985) 453–460

Received: December 20, 1984; accepted: March 26, 1985

# POLYFLUOROCYCLOALKENES. PART XVIII. ARYL ADDUCTS OF DECAFLUOROCYCLOHEXENE

Paul L. COE, David OLDFIELD and John Colin TATLOW

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

## SUMMARY

Decafluorocyclohexene reacted slowly with aniline to give 1-phenylamino-3-phenyliminoheptafluorocyclohex-1-ene, which was hydrolysed by hydrochloric acid to 3-phenylaminoheptafluorocyclohex-2-enone. Decafluorocyclohexene reacted stepwise with phenyl lithium, giving 1-phenylnonafluorocyclohexene and thence 1,2-diphenyloctafluorocyclohexene: the former product was attacked slowly by pentafluorophenyl lithium at -40°C affording 1-pentafluorophenyl-1-phenyloctafluorocyclohexene. Phenyl lithium reacted sluggishly with bis(pentafluorophenyl)octafluorocyclohexene to give 1-pentafluorophenyl-2-(2',3',5',6'-tetrafluoro-1'-biphenylyl)octafluorocyclohexene and 1,2-bis(2',3',5',6'-tetrafluoro-1'-biphenylyl)octafluorocyclohexene. 1,2-Diphenyloctafluorocyclohexene and 1,2-bis(pentafluorophenyl)octafluorocyclohexene were fluorinated by cobalt(III) fluoride to give the olefin, 1,2-bis(undecafluorocyclohexyl)octafluorocyclohexene.

## INTRODUCTION

This paper records further reactions [1] of decafluorocyclohexene (1) with nucleophiles. In particular, aryl species were used, to prepare precursors which might undergo further fluorination, leading to fluorocarbon fluids of relatively high molecular weight. The work extended that described in earlier papers, dealing with the reactions of decafluorocyclohexene with ammonia [2], and with methyl lithium [3].

0022-1139/85/$3.30 © Elsevier Sequoia/Printed in The Netherlands

## RESULTS AND DISCUSSION

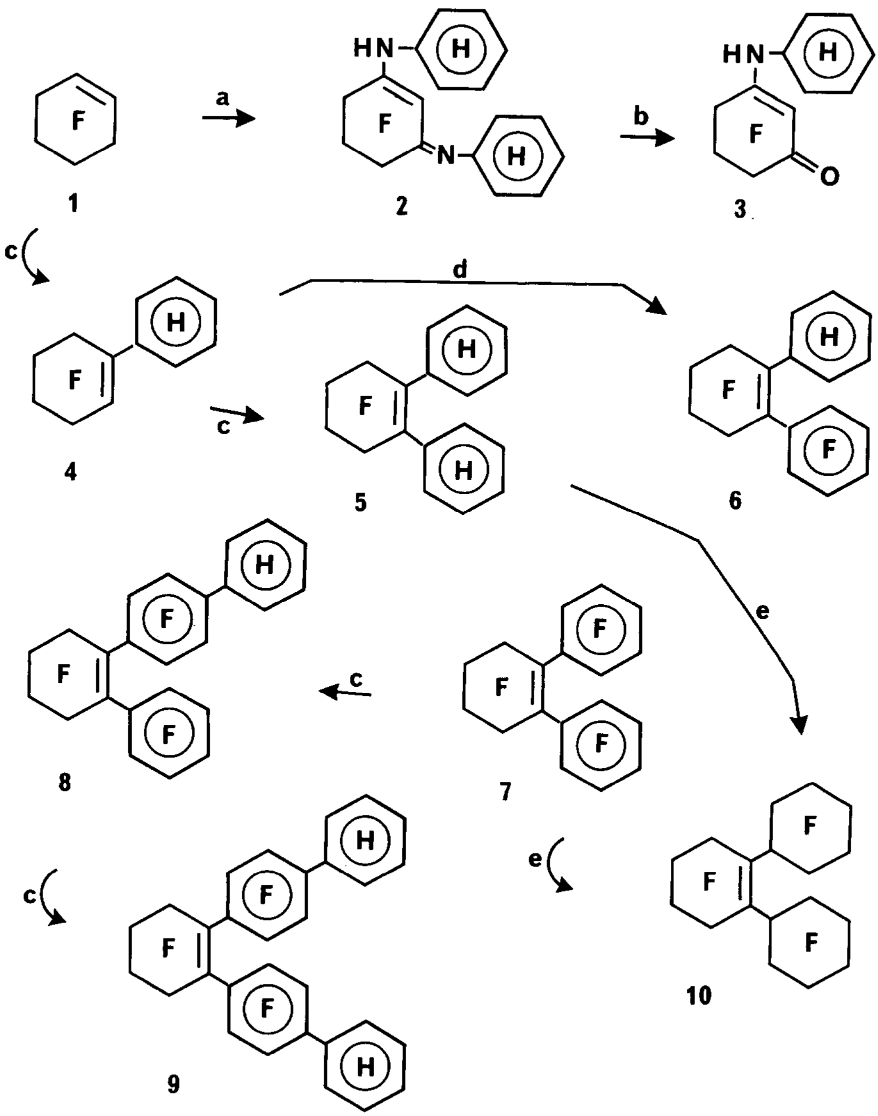
Analogously to the reactions with ammonia and alkylamines [2], decafluorocyclohexene (1) reacted with aniline, though only very slowly even under reflux. The product was 1-phenylamino-3-phenyliminoheptafluorocyclohex-1-ene (2; See Scheme). The structure was shown by the appropriate absorption bands in the infrared and ultraviolet due to conjugated unsaturation, and by oxidation with potassium permanganate in acetone. Though the presence of oxidation products of the aniline nucleus prevented the isolation of a pure specimen of its anilinium salt, hexafluoroglutaric acid was clearly formed. Hydrolysis of the imino-amine (2) was effected with hot hydrochloric acid. Though the reaction was slow, this was probably due mainly to insolubility of compound 2 in the medium. The product was 3-phenylaminoheptafluorocyclohex-2-enone (3); again the conjugated unsaturation gave rise to appropriate spectroscopic bands. More vigorous acidic hydrolysis of compound 2 liberated two molar proportions of aniline, but the parent keto-enol or diketone could not be isolated [*cf*. 1, 2].

All attempts to effect an analogous reaction between decafluorocyclohexene (1) and pentafluoroaniline were unsuccessful. Prolonged reaction in an autoclave at 280°C, or refluxing with stirring of a solution in diethyl ether in the presence of sodium hydride, gave no products, only recovered reactants.

One reaction between decafluorocyclohexene and an aryl lithium reagent has been reported already [4]: pentafluorophenyl lithium afforded 1-(pentafluorophenyl)nona-, and 1,2-bis(pentafluorophenyl)octa-fluorocyclohexene. When phenyl lithium and decafluorocyclohexene were reacted together in equimolar proportions, the major product was 1-phenylnonafluorocyclohexene (4), identical with the product made previously, by a copper-promoted crossed Ullman-type reaction [5] between bromobenzene and 1-bromononafluorocyclohexene. A minor product of this $C_6F_{10}$-PhLi reaction was 1,2-diphenyloctafluorocyclohexene (5); the structure was clearly established by the presence of only two $^{19}F$ nmr peaks ($\delta$, 109.1 and 134.8, of equal intensity; $\underline{CF_2}$-C=C and $CF_2\underline{CF_2}CF_2$ respectively).

Two molar proportions of phenyl lithium and $C_6F_{10}$ gave an increased proportion of product 5, but compound 4 still predominated: compound 4 and phenyl lithium gave compound 5, but again, the yield was poor.

1-Phenylnonafluorocyclohexene (4) was also treated with pentafluorophenyl lithium [4]. Since this decomposes near to room temperature *via*



REAGENTS : a, $PhNH_2$ : b, $HCl/H_2O$ : c, PhLi : d, $C_6F_5Li$ : e, $CoF_3$

SCHEME

tetrafluorobenzyne [4], a prolonged reaction at -40°C was necessary, but even so, the conversion to the only product found, 1-pentafluorophenyl-2-phenyloctafluorocyclohexene (6) was low. The structure was again clearly demonstrated by $^{19}F$ nmr peaks due to the octafluorocyclohexene residue at $\delta$ 110.9, 111.2 and 134.9, relative intensities 2:2:4, and from the pentafluorophenyl ring at 137.7, 149.4 and 160.3 relative intensities 2:1:2 [cf. 4].

In all of these reactions, the product mixtures were separated by column chromatography. Apart from traces of products arising from phenyl lithium itself, and recovered starting materials, the only compounds detected were 4, 5 or 6. These corresponded to exclusive replacement of the original vinylic fluorines of decafluorocyclohexene (1) or of its monophenyl adduct (4) by aryl groups in a simple addition-elimination pathway. The fluorine lost from the intermediate carbanion at each stage was that on the carbon at the original point of attack. No isomeric products arising from double bond migration (i.e. loss of fluorine from an $\alpha$-$CF_2$) were detected: traces might have been lost in the work-up, but, if any were formed the proportions must have been very small. This reaction of phenyl lithium in a specific manner is in contrast to additions to decafluorocyclohexene of alcohols [1] and metal hydrides [6] where up to 30% of an isomeric product can be isolated, arising from double bond shift. With methyl lithium, almost all of the products arose from simple addition-elimination, but there was some evidence for a trace of product arising from loss of fluorine from an $\alpha$-$CF_2$ with double bond shift.

The exclusive formation of products 4, 5, and 6 in the present reactions is presumably the result of a favourable decomposition pathway for the intermediate carbanion, arising from conjugation of the developing double bond with the aryl groups, in the styrene-type structure of 4, and in the cis-stilbene-type of 5 and 6. Easier accommodation of the relatively bulky aryl groups at a vinylic, rather than an allylic, centre of the polyfluorocyclohexene rings of the products may also be a relevant factor.

The action of phenyl lithium on the previously-mentioned 1,2-bis-(pentafluorophenyl)octafluorocyclohexene (7) was next studied. Again the reaction was sluggish, but two products were isolated by column chromatography. The first was 1-pentafluorophenyl-2-(2',3',5',6'-tetrafluoro-4'-biphenylyl)octafluorocyclohexene (8), as shown by a very weak ir band from a double bond of the type C-C=C-C, and $^{19}F$ nmr peaks typical of $>CF_2$ groups in an octafluorocyclohexene ring and of fluoro-aryl groups $C_6F_5$ and para-substituted X-$C_6F_4$-Y [cf. 4]. The second product was 1,2-bis(2',3',5',6'-

tetrafluoro-4-biphenylyl)octafluorocyclohexene (9), having $^{19}F$ nmr peaks from an octafluorocyclohexene, as for 8, and two sets of peaks due to aryl fluorines in ortho-positions. It is not surprising perhaps that nucleophilic attack on compound 7 occurs exclusively to eliminate the aryl fluorine in the para-position, and not at the hindered double bond. The para-fluorine was lost when octafluorotoluene reacted with $C_6F_5Li$ [4].

Fluorination of compounds 5 and 7 with cobalt(III) fluoride at 300°C or above gave the same product. Elemental analysis showed this to be 1,2-bis(undecafluorocyclohexyl)octafluorocyclohexene (10) and a very weak ir band confirmed the presence of the double bond. Failure to saturate this with fluorine is not entirely unexpected. Presumably two extra fluorines around the hindered double bond of compound 10 would cause steric interactions. Other examples of perfluoro-olefins resistant to further fluorination are known, e.g. dodecafluorobicyclo(3,3,0)oct-1(5)-ene [7].

## EXPERIMENTAL

### General

All reagents and solvents in the reactions involving organometallic species were rigorously dried using standard procedures. $^{19}F$ Nmr and $^{1}H$ Nmr measurements were made on a Perkin Elmer R10 machine, at 56.4 and 60 Mc/s respectively. Carbon tetrachloride was used throughout as solvent, and internal standards were $CCl_3F$ and $Si(CH_3)_4$ respectively. The $^{19}F$ signals all displayed fine structure, but only the basic chemical shift data was needed to determine the chemical constitution.

### Reaction of Decafluorocyclohexene (1) with Aniline

Redistilled aniline (20 $cm^3$) and decafluorocyclohexene (1) (10.0 g) were refluxed together with stirring for 88 hours. On being cooled, the product contained much solid aniline hydrofluoride, and was diluted with diethyl ether and well washed with water. The ether layer and ether extracts of the aqueous washings were dried ($MgSO_4$) and evaporated to leave a red oil. This was divided into 2 portions: one was chromatographed over alumina by elution with light petroleum (b.p. 60-80°C), the recovered solid being recrystallised from carbon tetrachloride to give yellow plates, m.p. 85-86°C: the second was dissolved in ether and washed well with 2M hydrochloric acid, the ether layer was dried ($MgSO_4$), and evaporated, and the residue recrystallised from carbon tetrachloride, to give yellow plates, m.p. 85-86°C. The two samples were isolated in comparable recoveries and were identical (mixed m.p. and spectroscopic parameters). Two recrystallisations of the combined product from carbon tetrachloride gave 1-phenylamino-3-phenyliminoheptafluorocyclohex-1-ene (2) nc (4.8 g), m.p. 88-89°C (Found: C, 55.7; H, 3.0. $C_{18}H_{11}F_7N_2$ requires C, 55.7, H, 2.9%); $\lambda_{max}$ (ethanol) 223, 241, 343 nm ($\varepsilon$ 13000, 10600, 16400 respectively); ir 1470 (s) 1530 (m), 1600 shoulder 1630 (m), 3200 (m) $cm^{-1}$.

## 3-Phenylaminoheptafluorocyclohex-2-enone (3)

The imino-amine (2) (1.0 g) and 50% hydrochloric acid (100 $cm^3$) were kept together on a boiling water bath for 5 hours, by which time the yellow starting material had been converted to a green solid. The mixture was cooled, the crystals filtered off, dried, and recrystallised from carbon tetrachloride to give light green 3-phenylaminoheptafluorocyclohex-2-enone (3) nc (0.6 g), m.p. 118-119°C (Found: C, 46.3; H, 1.9. $C_{12}H_6F_7NO$ requires C, 46.0; H, 1.9%); $\lambda_{max}$ (ethanol) 314.5 nm ($\varepsilon$ 24000); ir 1460 (s), 1530 (m), 1600 1630 double peak (s), 1690 (m), 3250 (m) $cm^{-1}$.

More vigorous hydrolysis of (2) (2.7 g) on a steam bath with stirring gave aniline (1.2 g), but the diketone could not be isolated.

## Reaction of Decafluorocyclohexene (1) with Phenyl Lithium

Phenyl lithium (8.4 g) in diethyl ether (104 $cm^3$) was added to decafluorocyclohexene (1) (26.2 g) in ether (100 $cm^3$) stirred at 0°C in an atmosphere of nitrogen. After being allowed to warm to 15°C, the mixture was kept for 2 hours at 15°C, with stirring throughout. The mixture was washed with 4M-hydrochloric acid (100 $cm^3$), and the ether layer, and ether extracts of the aqueous layer, were combined, dried ($MgSO_4$), and the ether distilled off through a 6" column to leave a brown oil (24.0 g). Separation of a portion (8.0 g) by glc (column 4.8 m x 35 mm packed with silicone gum 301 on Kieselguhr 1:6, $N_2$ flow rate 15 $lh^{-1}$, temp. 180°C) gave:- (i), benzene and bromobenzene (0.3 g); (ii), 1-phenylnonafluorocyclohexene (4) (4.5 g) identical with an authentic specimen [5]; (iii), diphenyl (0.1 g); (iv), an unknown liquid, one component only on analytical glc. Fraction (iv) deposited colourless crystals on standing, and recrystallisation from ethanol gave 1,2-diphenyloctafluorocyclohexene (5) nc (0.5 g), m.p. 42-43°C (Found: C, 57.2; H, 2.6. $C_{18}H_{10}F_8$ requires C, 57.15; H, 2.7%); $\lambda_{max}$ (ethanol) 253 nm ($\varepsilon$ 6110); ir 1680 (vw); $^1H$ nmr, $\tau$ 2.89 (s); $^{19}F$ nmr, $\delta$ 109.1, 134.8, intensity ratio 1:1.

Repetition of the experiment but using only half quantity (13.1 g) of decafluorocyclohexene (1) afforded crude product (22.5 g), all of which was separated as above to give the 1-phenyl-adduct (4) (8.0 g) and the 1,2-diphenyl-adduct (5) (2.5 g).

Phenyl lithium (1.25 g) in diethyl ether (15.5 $cm^3$) was added to 1-phenylnonafluorocyclohexene (4) (3.8 g) in ether (100 $cm^3$) stirred at 15°C in an atmosphere of nitrogen. After 2 hours, the mixture was refluxed for 2 hours further, and then worked up as above. Analytical glc showed the presence of compounds 4 and 5, and separation as before gave 5 (0.9 g) which crystallised, and was identical with the earlier samples.

### Reaction of 1-Phenylnonafluorocyclohexene (4) with Pentafluorophenyl Lithium

Butyl lithium (1.64 g) in *n*-hexane (10.3 $cm^3$) was added to pentafluorobenzene (4.3 g) in diethyl ether (50 $cm^3$) stirred at -78°C in an atmosphere of nitrogen. After 30 min., 1-phenylnonafluorocyclohexene (4) (8.2 g) in ether (50 $cm^3$) was added, and after stirring at -78°C for 1 hour, the reaction flask was tightly stoppered and kept at -40°C for 40 days. Work-up as before gave crude product (8.3 g), containing only two components by TLC. A portion (4.0 g) in light petroleum (b.p. 60-80°C) was chromatographed on silica gel, and eluted with more light petroleum. Two fractions were obtained, and after evaporation of solvent there resulted:- (i), starting material (4) (0.54 g); (ii), a white solid. This last was recrystallised from ethanol to give colourless needles of 1-pentafluorophenyl-2-phenyloctafluorocyclohexene (6) nc (0.75 g), m.p. 60-61°C (Found: C, 46.1; H, 0.8. $C_{18}H_5F_{13}$ requires C, 46.2; H, 1.1%); $\lambda_{max}$ (ethanol) 257 nm ($\varepsilon$ 2960); ir 1680 (vw); $^1H$ nmr, $\gamma$ 2.5-3.0 (m); $^{19}F$ nmr, $\delta$ 110.9, 111.2, 134.9, 137.7, 149.4, 160.3, relative intensities 2:2:4:2:1:2.

### Reaction of 1,2-Bis(pentafluorophenyl)octafluorocyclohexene (7) with Phenyl Lithium

Phenyl lithium (1.6 g) in diethyl ether (50 $cm^3$) was added to compound 7 [4] (5.0 g) in ether (80 $cm^3$) stirred at 15°C in a nitrogen atmosphere. After the mixture had been stirred under reflux for 4 hours, the reaction flask was tightly stoppered and kept at 15°C for 7 days. Isolation as before gave a brown oil (5.6 g). A portion of this (2.4 g) in light petroleum (b.p. 60-80°C) was chromatographed on silica gel, with elution by more light petroleum. Three fractions were obtained yielding three colourless solids after evaporation of solvent. The first was unreacted 7

(0.06 g), and the second was recrystallised from ethanol to give 1-pentafluorophenyl-2-(2',3',5',6'-tetrafluoro-1'-biphenylyl)octafluorocyclohexene (8) nc (0.08 g), m.p. 80-81°C (Found: C, 46.7; H, 0.6. $C_{24}H_5F_{17}$ requires C, 46.8; H, 0.8%); $\lambda_{max}$ (ethanol) 251 nm ($\epsilon$ 10800); ir 1675 (vw); $^1H$ nmr, $\gamma$ 2.58 (s); $^{19}F$ nmr, $\delta$ 111.1, 134.6, 137.1, 138.7, 140.9, 147.3, 158.9, relative intensities 4:4:2:2:2:1:2. The third solid was also recrystallised from ethanol, affording 1,2-bis(2',3',5',6'-tetrafluoro-1'-biphenylyl)octafluorocyclohexene (9) nc (0.17 g), m.p. 104-105°C (Found: C, 53.4; H, 1.5. $C_{30}H_{10}F_{16}$ requires C, 53.4; H, 1.5%); $\lambda_{max}$ (ethanol) 251 nm ($\epsilon$ 20900); no detectable band due to C=C in the ir; $^1H$ nmr, $\gamma$ 2.60 (s); $^{19}F$ nmr, $\delta$ 110.8, 134.5, 138.3, 141.0, relative intensities 1:1:1:1.

## 1,2-Bis(undecafluorocyclohexyl)octafluorocyclohexene (10)

The 1,2-diphenyl-adduct (5) (2.0 g) was fluorinated by passage over cobalt(III) fluoride (150 g) at 320°C in a small stirred reactor (460 mm x 44 mm diam.). Compound 5 was put into the reactor as a finely ground solid through a wide-bore tap and swept on by a nitrogen stream (2.0 $lh^{-1}$). The total addition took 2 hours, and the nitrogen sweep continued for 2 hours further. The colourless liquid product was distilled to give 1,2-bis(undecafluorocyclohexyl)octafluorocyclohexene (10) nc (1.4 g) b.p. 260°C (Found: C, 27.6; F, 72.2. $C_{18}F_{30}$ requires C, 27.5; F, 72.5%); ir 1630 (vw).

Fluorination of the bispentafluorophenyl analogue (7) at 300°C also gave compound 10 (1.8 g), identical with the above material.

## REFERENCES

1 Part XVII of this Series; R.G. Plevey, D.J. Sparrow and J.C. Tatlow, J. Fluorine Chem., 26 (1984) 515.

2 P. Robson, J. Roylance, R. Stephens, J.C. Tatlow and R.E. Worthington, J. Chem. Soc., (1964) 5748.

3 D.R. Sayers, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1964) 3035.

4 D.D. Callander, P.L. Coe and J.C. Tatlow, Tetrahedron, 22 (1966) 419.

5 G. Camaggi, S.F. Campbell, D.R.A. Perry, R. Stephens and J.C. Tatlow, Tetrahedron, 22 (1966) 1755.

6 D.E.M. Evans, W.J. Feast, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1963) 4828.

7 J.A. Oliver, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 6 (1975) 19.