Tetrahedron, 1960, Vol. 9, pp. 240 to 245. Pergamon Press Ltd. Printed in Northern Ireland

AROMATIC POLYFLUORO-COMPOUNDS—V*

THE PREPARATION OF HIGHLY FLUORINATED BENZENES BY DEFLUORINATION OF POLYFLUOROCYCLOHEX-ANES, -ENES, AND -DIENES

P. L. Coe, C. R. Patrick and J. C. Tatlow
Chemistry Department, The University, Birmingham

(*Received* 4 *December* 1959)

Abstract—Hexa-, penta- and tetra- fluorobenzenes are formed from appropriate polyfluorocyclohexanes, -enes and -dienes by passage in vapour form over heated iron gauze.

In previous communications[1,2] we have described a new general method for the preparation of perfluoro-aromatic compounds by the defluorination of cyclic aliphatic fluorocarbons. The method consists in passing the compound to be defluorinated, in the vapour phase, in a stream of nitrogen, over a heated metal, usually iron or nickel gauze, packed into a tubular reaction vessel.[2] The metal fluoride which is produced in the defluorination process forms an impervious deposit on the metal surface and eventually prevents further reaction. The metal needs, therefore, to be regenerated, and this may conveniently be done by reduction of the metal fluoride with hydrogen. In this paper we describe the extension of this method of defluorination to the preparation of hexafluorobenzene from dodecafluorocyclohexane and from decafluorocyclohexene, and to the preparation of other highly fluorinated benzenes, particularly of pentafluorobenzene, from various fluorocyclohex-enes and -dienes.

The formation of perfluoroaromatic compounds by the defluorination of saturated materials depends on the greater stability of the aromatic compounds to the defluorination conditions. Thus, at low temperatures, depending on the contact time but generally about 350° or less, no defluorination of alicyclic compounds takes place, whereas at high temperatures, about 750° or more, fluorocarbon material is completely broken down, presumably to give metal fluoride and carbon. Simple considerations, therefore, suggest that for each compound investigated there should be a reaction contact time and reactor temperature for which the yield of the desired aromatic compound is optimal. These reaction conditions will, in addition, be determined by the geometry of the reactor and its packing, and also by the age and previous treatment of the packing. The effect of temperature on the defluorination process is illustrated by the results on the defluorination of decafluorocyclohexene[3] (Table 1). These results show that the most economical temperature for the production of hexafluorobenzene in the reactor used was about 550°. At this temperature the total recovery of material by weight was about 70 per cent, and about 46 per cent of the starting material was converted to hexafluorobenzene.

---

* Part IV: *J. Chem. Soc.* In press.

[1] B. Gething, C. R. Patrick, J. C. Tatlow, R. E. Banks, A. K. Barbour and A. E. Tipping, *Nature, Lond.* **183**, 586 (1959).

[2] B. Gething, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature, Lond.* **183**, 588 (1959).

[3] A. K. Barbour, H. D. Mackenzie, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* **4**, 347 (1954).

It has been found possible to defluorinate dodecafluorocyclohexane[4] to give hexafluorobenzene. Decafluorocyclohexene is also a product of the reaction, particularly at relatively low temperatures. This observation demonstrates the stepwise nature of the defluorination process. The failure to observe octafluorocyclohexadienes in the reaction products is obviously the consequence of the extreme instability of these compounds to the defluorination conditions needed to defluorinate more nearly saturated compounds. Octafluorocyclohexadienes[5] have been found to give hexafluorobenzene almost exclusively and in good yield (over 90 per cent) at temperatures between 400 and 450° using nitrogen flow rates of 2 litres/hr. Reactor temperatures greater than about 550° were found to be necessary for the defluorination of decafluorocyclohexene and dodecafluorocyclohexane.

TABLE 1. EFFECT OF TEMPERATURE ON THE DEFLUORINATION OF DECAFLUOROCYCLOHEXENE

Nitrogen flow rate 2 l/hr. Charge of C_6F_{10}, 16·6 g in each case. Only C_6F_{10} and C_6F_6 were found in the products.

Reactor temperature (°C)	Weight of material recovered (g)	% C_6F_6 in product
490	13·17	11·7
510	12·44	36·1
530	11·15	43·6
550	10·91	62·9
580	8·43	73·0
600	6·58	ca 100

TABLE 2. DEFLUORINATION OF DODECAFLUOROCYCLOHEXANE

Temperature (°C)	Flow rate (l/hr)	Input (g)	Yield (g)	Wt. of products isolated (g)	
				C_6F_{12} $+C_6F_{10}$	C_6F_6
630	8	6·5	4·3	2·5	0·5
590	6	5·5	2·7	1·1	1·0
590	4	21	9·5*	4·4*	1·6*

* In this experiment only 7·2 g of the mixed product was carried forward to separation. The weight of product reported as C_6F_{12}/C_6F_{10} contained 0·2 g of C_6F_{10}.

Early experiments showed that the defluorination process was not limited in its application to compounds containing only carbon and fluorine. Thus, 1H-heptafluorocyclohexa-1,3-diene[6] was found to give pentafluorobenzene together with

---

[4] R. P. Smith and J. C. Tatlow, *J. Chem. Soc.* 2505 (1957).

[5] D. E. M. Evans and J. C. Tatlow, *J. Chem. Soc.* 1184 (1955).

[6] J. Godsell, M. Stacey and J. C. Tatlow, *Tetrahedron* **2**, 193 (1958).

hexafluorobenzene which was probably produced by the dehydrofluorination of 5H-heptafluorocyclohexa-1,3-diene or a similar structure formed by the isomerization of the starting material. 1,3- and 1,4-Dienes isomerize readily when heated.[1] Since hexafluoro- and pentafluoro-benzene may easily be separated by preparative scale gas chromatography the defluorination reaction affords a convenient method for the preparation of the pentafluoride. Further investigations have been made of the

Table 3. Defluorination of mixed octafluorocyclohexadienes
Results calculated for charges of 16·6 g

Temperature (°C)	Flow rate (l/hr)	Weight of material recovered (g)
450	4	12·6*
500	4	10·8
540	4	10·6
580	4	9·2
600	4	5·7
400	2	12·0
450	2	10·7
470	2	9·8
500	2	8·8

Except where indicated, the recovered material was almost pure hexafluorobenzene.

These results indicate that an increase in reaction time brought about by reduction of the flow rate reduces the temperature required to give optimum yields of aromatic products.

* This product contained about 10 per cent starting material.

Table 4. Defluorination of heptafluorocyclohexadienes
Variation of products with temperature of the body of the reactor. Flow rate 2 l. nitrogen/hr. Charge 16·6 g.

Temperature (°C)	Weight of material recovered* (g)	% C_6F_5H
390	12·1	57
400	12·1	60
420	12·1	68
450	12·0	64
460	9·9	65
480	10·5	64
500	9·9	61

* The recovered product contained only hexafluoro- and pentafluorobenzene in all cases.

defluorination of heptafluorocyclohexadienes, and it has been found that over a wide range of reactor temperatures the ratios of the amounts of pentafluorobenzene to hexafluorobenzene in the products were close to two to one, although the overall yield of these compounds decreased at temperatures above about 450° using nitrogen flow rates of 4 litres/hr. It was found, however, that the composition of the reaction products was influenced by the distribution of temperature in the reactor, rather than by the temperature of the central and most extensive zone of the reactor. This point is illustrated by the results presented in Table 5, which were obtained by the defluorination of the mixture of heptafluorocyclohexadienes, prepared by the dehydrofluorination of 1H, 2H, 4H-nonafluorocyclohexane,[6] and which contained 1H-heptafluorocyclohexa-1,4-diene (about two parts), 1H-heptafluorocyclohexa-1,3-diene (about one part) and 2H-heptafluorocyclohexa-1,3-diene (about one part). These results show that higher temperatures in the first part of the reactor to be encountered by the starting material favour the formation of pentafluorobenzene relative to hexafluorobenzene. This effect may be understood in terms of the competition between isomerization and defluorination as the first process in the reaction system. If a mixture of dienes is subjected first to temperatures that are too low to enable defluorination to take place, the more facile isomerization may proceed to produce compounds in which hydrogen is attached to saturated carbon atoms, and these will readily lose hydrogen fluoride to give, from heptafluorocyclohexadienes, hexafluorobenzene. At higher temperatures defluorination of the dienes will proceed more readily to give pentafluorobenzene, and will reduce the proportion of hexafluorobenzene in the product.

TABLE 5. DEFLUORINATION OF MIXED HEPTAFLUOROCYCLOHEXADIENES USING VARIOUS REACTOR CONDITIONS

Nitrogen flow rate 4 l/hr. Charge of dienes 16·6 g in each case.

Reactor temperature (°C)					Weight of material recovered (g)		
Section No.					Total	C_6F_6	C_6F_5H
1	2	3	4	5			
120[†]	460	460	460	130	12·6	5·1	5·1
345	460	460	460	390	13·5	6·8	3·2
460	460	460	400	380	10·3	1·6	6·2[*]
460	460	460	400	380	10·7	1·8	6·1

[*] The products of this run also included 0·7 g of 1,2,4,5-tetrafluorobenzene. The starting material was found to be free of dienes containing two hydrogen atoms, and the tetrafluorobenzene presumably resulted from reduction by hydrogen adsorbed in the reactor. Similar observations have been made in some other cases and the effect is being investigated further.

[†] Presumably in this case the temperature in the first section is too low to produce much reaction.

The competition between isomerization and defluorination as first reaction steps, also accounts for the effects observed on passing successive samples of mixed hepta-fluoro-1,3- and 1,4-dienes through the reactor without removal of the metal fluoride by hydrogenation between the runs. The product obtained from the defluorination of a second aliquot of the mixed dienes contained 40 per cent pentafluorobenzene and

60 per cent hexafluorobenzene, whereas the first aliquot produced 60 per cent pentafluorobenzene and 40 per cent hexafluorobenzene. The difference between the products is due to the formation of a fluoride deposit on the metal in the first run so as to reduce the ease of defluorination, and so raise the probability of isomerization as first reaction step in the second run. It is for this reason that the use of large aliquots produces lower yields of pentafluorobenzene.

The defluorination reaction was applied to mixed 1H,2H-hexafluorocyclohexa-1,4- and 1,3-dienes[7] to give a mixture of pentafluorobenzene and 1,2,3,4-tetrafluorobenzene, the first compound arising presumably from the dehydrofluorination of an isomer of the starting material produced under the reaction conditions.

The defluorination of 4H-nonafluorocyclohexene[5] yielded both pentafluorobenzene and hexafluorobenzene, but mainly the former. Thus, at 450° using a nitrogen flow rate of 2 litres/hr, the products of the reaction were pentafluorobenzene (33 per cent), and hexafluorobenzene (10 per cent), both calculated on the basis of yield from starting material. The hexafluorobenzene is produced by the successive dehydrofluorination and defluorination of the starting material. It is noteworthy that the temperatures required to defluorinate nonafluorocyclohexene (450–500°) are lower than those required to defluorinate decafluorocyclohexene (550–600°), and probably reflect the lower strength of C—F bonds in $>$CHF groups relative to those in $>CF_2$ groups.

Undecafluorocyclohexane[3] was found on pyrolytic defluorination to give hexafluorobenzene and pentafluorobenzene. The first of these compounds, whose formation involves dehydrofluorination, was formed in the greater yield.

TABLE 6. DEFLUORINATION OF 1H,4H-OCTAFLUOROCYCLOHEX-1-ENE
Runs at 2 l. nitrogen/hr. 8·2 g charge. The product contained 1,2,4,5-tetrafluorobenzene in all cases.

Temperature (°C)	Yield (g)	% C_6F_6	% C_6F_5H	% $C_6F_4H_2$
420	4·5	15	54	15
480	4·3	24	33	21
550	3·3	15	37	26

The defluorination of 1H,4H-octafluorocyclohexene[7] has been found to produce 1,2,4,5-tetrafluorobenzene, pentafluorobenzene and hexafluorobenzene. Also, as noted for the case of nonafluorocyclohexene, the temperatures needed for the reaction of this compound (about 450°) are lower than those required for the defluorination of decafluorocyclohexene. A similar reaction with 4H/5H-octafluorocyclohexene[6] has been found to give 1,2,3,4-tetrafluorobenzene together with some pentafluoro- and hexafluoro-benzene.

In the course of this work the metal packing used in the reactors was iron gauze. As an alternative packing the use of nickel shot was tried, but this gave erratic results, and examination after a short period of use showed that the shot had sintered together so as to favour channelling of the gas passed through the reactor, and the packing could be removed from the reactor only with considerable difficulty. It was also

---

[7] R. Stephens, J. C. Tatlow and E. H. Wiseman, *J. Chem. Soc.* 148 (1959).

observed that saturated fluoro-compounds were not readily defluorinated by a packing of new iron gauze, but the efficiency of the packing at first increased with use, and then became steady. This ageing effect was not so marked in respect of defluorination of the octafluorocyclohexadienes.

EXPERIMENTAL

Apparatus. The reactors used in this investigation were the same as those described elsewhere[2] and consisted of nickel tubes of diameter 2½″ and length 4′ mounted in horizontal furnaces and packed with iron gauze. The furnaces, which were of the same length as the reactor tubes, consisted of five heating sections of equal length. The flow rate of the incoming gas stream was measured on a rotameter. The samples were volatilized into the stream of nitrogen in a heated section of glass tubing close to the furnace. The reaction products were collected in traps immersed in liquid oxygen, and were separated by use of preparative scale chromatography.[8] After each run, except where otherwise indicated, the metal fluoride formed in the reactor was removed by passage of a stream of hydrogen flowing at 10–20 litre/hr for 30 min, followed by a stream of nitrogen flowing at 8 litre/hr for a further 30 min.

Defluorination of successive charges of mixed heptafluoro-cyclohexadienes without intermediate removal of fluoride layer

The mixed heptafluorodienes (16·5 g) were passed in a stream of nitrogen at 4 litres/hr through the reactor heated in the various sections to 460°, 460°, 460°, 400°, and 380° respectively from the inlet end. The product (11·6 g) contained hexafluorobenzene (37%) and pentafluorobenzene (63%). A second charge of dienes passed through the reactor under the same conditions gave a product (11·2 g) containing hexafluorobenzene (61%) and pentafluorobenzene (39%).

Defluorination of 1H,2H-*hexafluorocyclohexa*-1,4- *and* -1,3- *diene*

A mixture of the dienes (8 g) was passed through the reactor at 450° in a stream of nitrogen at 2 litre/hr. The product (5·3 g) contained pentafluorobenzene (49%) and 1,2,3,4-tetrafluorobenzene (51%).

Defluorination of 4H-*nonafluorocyclohexene*

The 4H-nonafluorocyclohexene (16 g) was passed through the reactor at 450° in a stream of nitrogen flowing at 2 litre/hr. The product (12·2 g) contained hexafluorobenzene (10%), pentafluorobenzene (33%), and unchanged starting material.

Defluorination of 4H/5H-*octafluorocyclohexene*

The 4H/5H-octafluorocyclohexene (8·2 g) was passed through the tube at 520° in a stream of nitrogen flowing at 2 litre/hr. The product (1·74 g) contained 1,2,3,4-tetrafluorobenzene (87%) and a mixture of hexafluoro- and pentafluoro-benzene (13%).

Defluorination of undecafluorocyclohexane

Undecafluorocyclohexane (5 g) was passed through the reactor, maintained at 530°, in a stream of nitrogen flowing at 2 litre/hr. The product (1 g) was found to contain decafluorocyclohexene (17%), hexafluorobenzene (50%) and pentafluorobenzene (33%).

Identification of products

Products were identified by analytical gas chromatography and by the identity of the infra-red spectra of the pure components with those of authentic specimens. The 1,2,3,4-tetrafluorobenzene was identical with material synthesized by Wall[9] and with a specimen made here by an independent route.[10]

Acknowledgements—The authors thank Professor M. Stacey, F.R.S., for his interest, Dr. K. J. Morgan for the infra-red spectra, and Dr. L. A. Wall for the sample of 1,2,3,4-tetrafluorobenzene. One of us (P. L. C.) is indebted to British Industrial Plastics Limited for a scholarship.

---

[8] D. E. M. Evans, W. E. Massingham, M. Stacey and J. C. Tatlow, *Nature, Lond.* **182**, 591 (1958).

[9] W. J. Pummer, R. E. Florin and L. A. Wall, *J. Res. Nat. Bur. Stand.* **62**, 113 (1959).

[10] E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* forthcoming publication.