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THE VAPOUR PHASE FLUORINATION OVER COBALTIC FLUORIDE OF THE ISOMERIC DICHLOROBENZENES

CHLOROFLUOROCYCLOHEXANES AND THEIR REACTIONS

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Abstract—The exhaustive fluorination of the isomeric dichlorobenzenes gives mixtures of dodecafluorocyclohexane, chloroundecafluorocyclohexane, the isomeric dichlorodecafluorocyclohexanes, and the isomeric trichlorononafluorocyclohexanes. These products have been separated and mixtures of two latter sets of isomers have been reduced with $LiAlH_4$ to give fluorocyclohexanes of known structure. The fluorinations of these starting materials are evidently accompanied by extensive intra- and intermolecular migration of chlorine, and by some displacement of chlorine. The pyrolytic dehalogenation over iron of chloroundecafluorocyclohexane gives decafluorocyclohexene in good yield. From the dichloro- and trichlorocyclohexanes, octafluorocyclohexadienes, and mixture of new chlorononafluorocyclohexenes, hexafluorobenzene and pentafluorobenzene, have been formed on pyrolysis over iron.

Earlier work in these laboratories[1] showed that the products of fluorination of *o*-dichlorobenzene over cobaltic fluoride contained dodecafluorocyclohexane, chloroundecafluorocyclohexane, and what was later shown to be a mixture of dichlorodecafluorocyclohexanes.[1,2] A more detailed study of the fluorination of dichlorobenzenes has been carried out, both in order to discover more about the migration and displacement of chlorine that occurs during the reaction, and in order to study the pyrolytic behaviour of the reaction products.

The fluorination of *o*-, *m*- and *p*-dichlorobenzenes with cobaltic fluoride yields mixtures of the same group of products, but the proportions of these depend on the nature of the starting material. The mixtures obtained have been separated by fractional distillation and preparative gas chromatography to give dodecafluorocyclohexane, chloroundecafluorocyclohexane, a mixture of dichlorodecafluorocyclohexanes, and a mixture of trichlorononafluorocyclohexanes. Under the conditions used for fluorination only trivial amounts of other products were obtained. The mixtures of the isomeric chlorofluorocyclohexanes could not be separated using various stationary phases on gas chromatography, or by any other means.[3] The products of fluorination had the compositions given in Table 1. These results demonstrate that extensive migration of chlorine has taken place during fluorination. Although the reaction conditions used were similar, the migration of fluorine was the more extensive in the fluorination of *o*-dichlorodecafluorocyclohexane. Comparison of the yields of several chlorofluoro-compounds shows that the extent of loss of chlorine was least in the fluorination of *o*-dichlorobenzene. This observation is consistent with the trends shown by the weights of crude products recovered from the fluorinations. The fluorination of 1,2-dichlorocyclohexane also shows extensive

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[1] R. E. Worthington and J. C. Tatlow, *J. Chem. Soc.* 1251 (1952).
[2] J. Roylance, R. E. Worthington and J. C. Tatlow, *J. Chem. Soc.* 4426 (1954).
[3] R. D. Chambers, J. Heyes, and W. K. R. Musgrave, *Tetrahedron* **19**, 891 (1963).

intermolecular migration of chlorine, yielding dodecafluorocyclohexane (29%), chloroundecafluorocyclohexane (34%), dichlorodecafluorocyclohexanes (23%) and trichlorononafluorocyclohexanes (11%). A full examination of these products has not been carried out.

Table 1. Percentage composition of products of fluorination reactions

Starting material	o-$C_6H_4Cl_2$	m-$C_6H_4Cl_2$	p-$C_6H_4Cl_2$
Product			
C_6F_{12}	7	28	22
$C_6F_{11}Cl$	28	36	35
$C_6F_{10}Cl_2$	39	25	27
$C_6F_9Cl_3$	21	7	9
Others	5	4	7

A fuller examination of the products from the dichlorobenzene was made by reducing the chlorine-containing compounds to the corresponding hydrogen-containing compounds by reaction with lithium aluminium hydride.[2] The products of reduction of the mixture of dichlorodecafluorocyclohexane were separated by gas chromatography into the following fractions: (i) 1H/2H-decafluorocyclohexane; (ii) a mixture of 1H/3H- and 1H/4H-decafluorocyclohexanes; (iii) 1H,4H/-decafluorocyclohexane; (iv) 1H,2H/-decafluorocyclohexane; and (v) 1H,3H/-decafluorocyclohexane. The second of these fractions was analysed for its two components by measuring the areas under the respective NMR peaks. On the justifiable assumption that no migration occurs in the replacement of chlorine by hydrogen[2] the mixtures of dichlorodecafluorocyclohexanes obtained by the fluorination of the different starting materials were shown to have the compositions given below, demonstrating that extensive intramolecular migration of chlorine had effectively taken place during fluorination. The indicated proportions of 1,2-, 1,3- and 1,4-dichloro-compounds were 54, 21, 25%, 28, 40, 32% and 21, 26 and 53% from *o*-, *m*- and *p*-dichlorobenzenes respectively.

Like reduction of the mixtures of isomeric trichlorononafluorocyclohexanes obtained from the fluorination products gave mixtures of nonafluorocyclohexanes. These mixtures were separated by gas chromatography into the following fractions: (i) 1H,4H/2H-nonafluorocyclohexane; (ii) a mixture of 1H,2H/3H- and 1H,3H/2H-nonafluorocyclohexanes; (iii) 1H,2H/4H-nonafluorocyclohexane; (iv) 1H/2H,4H-nonafluorocyclohexane; (v) 1H,2H,4H/-nonafluorocyclohexane; (vi) 1H,2H,3H/-nonafluorocyclohexane; and (vii) a mixture of unidentifiable products (about 15–20%). No products arising from 1,3,5-trichlorononafluorocyclohexanes were identified. These may be concealed in the mixture of unidentifiable products. From the quantities of products isolated and identified it is evident that about 16%, 14% and 9% arise from 1,2,3-trichlorononafluorocyclohexanes in the fluorination products of *o*-, *m*- and *p*-dichlorobenzenes respectively, and that the remainder arise from 1,2,4-trichlorononafluorocyclohexanes.

The dehalogenation of chlorofluorocyclohexanes containing more than four chlorine atoms per molecule and produced by the fluorination of hexachlorobenzene,

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[2] G. M. Brooke, R. D. Chambers, J. Heyes and W. K. R. Musgrave, *J. Chem. Soc.* 729 (1964).

has been reported.[5] Dehalogenation over heated iron of chloroundecafluorocyclohexane gives almost exclusively decafluorocyclohexene, and this reaction proceeds more readily at lower temperatures than does the defluorination of dodecafluorocyclohexane. Although further defluorination of decafluorocyclohexane is possible, it proceeds only with difficulty and inefficiently.[6] Mixtures of dichlorodecafluorocyclohexanes defluorinate readily over heated iron to give mixtures of decafluorocyclohexene, small amounts of isomeric octafluorocyclohexadienes and of chlorononafluorocyclohexanes, and larger amounts of hexafluorobenzene. Pentafluorobenzene is also formed, presumably by reduction of chlorine in the reaction intermediates by hydrogen adsorbed in the pyrolysis tubes, since the product was formed despite the absence of hydrogen from the starting material. Although hydrogen-containing materials have been found in the products of pyrolysis under like conditions of perfluorocyclohexanes the amounts have been very small. Chlorine thus appears to be more readily reduced than does fluorine in such compounds. This is consistent with some findings in the reduction of simpler halogenated compounds using hydrogen with palladium catalysts.[7]

Mixtures of trichlorononafluorocyclohexanes are readily dehalogenated over heated iron to give a mixture of compounds. The products formed at lower temperatures are, with the omission of decafluorocyclohexene, which would not be an anticipated product from these starting materials, the same as those obtained from dichlorodecafluorocyclohexanes. At higher temperatures hexafluorobenzene and pentafluorobenzene are formed almost exclusively. The dehalogenation of these compounds must be determined not only by their content of chlorine, but also by the disposition of the substituent atoms. Compounds containing the 1,2-dichloro-group are likely to be dechlorinated readily to a cyclohexene structure. If this were to be decafluorocyclohexene, further dehalogenation would be difficult.

EXPERIMENTAL

Fluorinations. These were carried out in the manner described previously,[8] using, however, in some cases a larger reactor (containing 6 kg CoF_3). The products were condensed in Ni traps cooled with solid Co_2, and were separated, after washing with water, by fractional distillation followed by preparative gas chromatography using dinonyl phthalate, silicone gum, or Kel-F oil as stationary phases. The fluorination of 340 g *o*- and *p*-dichlorobenzenes at 300° gave respectively 680 and 560 g crude product. Similarly 330 g *m*-dichlorobenzene gave 510 g crude products.

Reduction of chlorofluoro-compounds. Reduction of the several fractions of chlorofluorocyclohexanes were effected with $LiAlH_4$.[9] The crude products, dissolved in ether were separated by preparative gas chromatography using dinonyl phthalate as stationary phase. The separated components were identified by comparison of their IR and NMR spectra with those of authentic specimens.

Pyrolytic dehalogenation of chlorofluorocyclohexanes. Portions of the compounds (1–10 g) were passed through a Ni tube (length 3′, diam 2½″) contained in a furnace and packed with pieces of Fe gauze. The products were collected in traps immersed in liquid air, and were separated by preparative gas chromatography using dinonyl phthalate as stationary phase. Examples are given below.

Chloroundecafluorocyclohexane (5·2 g) was passed in a stream of N_2 (flow rate 2 l/hr) through the pyrolysis tube heated to 400°. Of the products (3·7 g) a portion (3·3 g) was separated to give decafluorocyclohexene (2·8 g). At temps above about 400° extensive destruction of compound took place, and at lower temps appreciable amount of starting material was recovered. Thus at

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[5] R. H. Mobbs and W. K. R. Musgrave, *Chem. & Ind.* 1268 (1961).

[6] P. L. Coe, C. R. Patrick and J. C. Tatlow, *Tetrahedron* **9**, 240 (1960).

[7] J. R. Lacher, A. Kianpour, F. Oelting and J. D. Park, *Trans. Farad. Soc.* **52**, 1500 (1956).

[8] A. K. Barbour, G. B. Barlow and J. C. Tatlow, *J. Appl. Chem.* **2**, 127 (1952).

250° only 10% conversion to decafluorocyclohexene was effected, and the balance of the unreacted chloroundecafluorocyclohexane was recovered in good yield.

A mixture of dichlorodecafluorocyclohexanes (5 g) was passed through the pyrolysis tube in a stream of N_2 (flow rate 2 l/hr) at 250°. Of the products (4·0 g) a portion (1·7 g) was separated to give decafluorocyclohexene (0·52 g), and a mixture of octafluorocyclohexa-1,3-diene and chlorononafluorocyclohexene (0·56 g). The separation of the latter mixture is described below.

At 300°, using the same flow rate of N_2, dichlorodecafluorocyclohexane (5 g) gave a mixture (2·8 g), a portion of which (2·7 g) was separated to give decafluorocyclohexene (0·8 g), octafluorocyclohexa-1,4-diene (0·1 g), and the mixture of chlorononafluorocyclohexene and octafluorocyclohexa-1,3-diene mentioned above (0·5 g). Similarly at 450° the dichloro-compound (10 g) gave a mixture (3·8 g), a portion of which (2·6 g) was separated to give decafluorocyclohexene (0·8 g), hexafluorobenzene (0·8 g) and pentafluorobenzene (0·3 g).

Trichlorononafluorocyclohexane (5 g) passed through the tube in a stream of N_2 (flow rate 2 l/hr) at 300° gave a mixture (2·8 g) which was separated to give octafluorocyclohexa-1,4-diene (0.3 g), and the mixture of octafluorocyclohexa-1,3-diene and chlorononafluorocyclohexene described below (1·4 g). Trichlorononafluorocyclohexane (5 g) in a stream of N_2 (10 l/hr) at 400° gave a mixture (2·6 g) which was separated to give octafluorocyclohexa-1,4-diene (0·4 g), a mixture of octafluorocyclohexa-1,3-diene and chlorononafluorocyclohexene (0·7 g), hexafluorobenzene (0·4 g) and pentafluorobenzene (0·1 g).

*Separation of mixtures of octafluorocyclohexa-*1,3*-diene and chlorononafluorocyclohexene.* Mixtures of these two compounds were separated from the products of a number of pyrolysis experiments such as those described above. The two components could be separated using Kel-F oil (M.M.M. Co.) as stationary phase in gas chromatography. The proportions of the two components in the mixtures depended on the sources of the mixtures. Chlorononafluorocyclohexene (almost certainly a mixture of isomers) was characterized by its analysis (C, 25·8; F, 60·9; Cl, 12·3. C_6F_9Cl requires: C, 25·8; F, 61·4; Cl, 12·7%), and its mass spectrometric cracking pattern (principal mass peaks 278, C_6F_9Cl; 259, C_6F_8Cl; 243, C_6F_9).

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