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THE PYROLYTIC REACTIONS OF PERFLUOROISOPROPYLCYCLOHEXANE AND OF SOME PERFLUORODICYCLOHEXYL ALKANES

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Abstract—The action of heat on perfluoroisopropylcyclohexane, perfluoro-dicyclohexylmethane, -1,2-dicyclohexylethane and -1,4-dicyclohexylbutane, gives a range of products among which octafluorocyclopentene and decafluoro-1-methylcyclopentene are prominent. These reactions proceed so readily as to prevent the formation of aromatic fluorocarbons by defluorination. Of the compounds studied only perfluoroisopropylcyclohexane has been defluorinated to give decafluoro-α-methylstyrene.

THE defluorination of highly fluorinated cyclohexanes and similar compounds gives highly fluorinated benzenes,[1-3] generally in good yield, although small amounts of breakdown products formed in competing reactions have been observed in some cases.[4,5] We now report the attempted extension of the defluorination reaction to perfluoroisopropylcyclohexane, perfluorodicyclohexylmethane, perfluoro-1,2-dicyclohexylethane, and perfluoro-1,4-dicyclohexylbutane. Only in the case of perfluoroisopropylcyclohexane has an aromatic product, perfluoro-α-methylstyrene, been obtained. There is a competing facile decomposition of the alicyclic perfluorocarbons to give decafluorocyclohexene and perfluorinated derivatives of cyclopentane, and these are the major products in the other cases.

The pyrolysis of perfluorodicyclohexylmethane over nickel gauze at 500° or below resulted in little or no reaction, and the starting material was recovered in good yields. At higher temperatures (about 550°) reaction took place to produce a mixture of solid and liquid fluorocarbons. At yet higher temperatures only liquid products were obtained. At all temperatures a considerable amount of low-boiling material, shown by IR spectrometry to be largely hexafluoroethane, was formed. The solid constituent of the products was starting material. Gas chromatography using dinonylphthalate as stationary phase, resolved the liquid product into two components, the longer retained of which was decafluoro-cyclohexene. The major component was a mixture, and this was separated by gas chromatography, using a saturated fluorocarbon (perfluorodicyclohexylmethane, perfluoro-1,2-dicyclohexylethane, or perfluoroperhydroanthracene) as stationary phase, into two constituents. Samples sufficient in size to allow characterization were obtained. One product was octafluorocyclopentene, and the second, an unknown olefin, was shown by mass spectrometry, to be a decafluoromethylcyclopentene. The low-lying position of its olefinic IR absorption peak (1725 cm^{-1} compared with 1773 cm^{-1} in octafluorocyclopentene[6]) suggested that

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[1] B. Gething, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature, Lond.* **183**, 588 (1959).
[2] P. L. Coe, C. R. Patrick and J. C. Tatlow, *Tetrahedron* **9**, 240 (1960).
[3] J. Burdon, D. J. Gilman, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature, Lond.* **186**, 231 (1960).
[4] C. R. Patrick, A. E. Pedler, A. Seabra, R. Stephens and J. C. Tatlow, *Chem. & Ind.* 1557 (1963).
[5] R. E. Banks, W. M. Cheng and R. N. Haszeldine, *J. Chem. Soc.* 3407 (1962).
[6] R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 281 (1963).

the compound was decafluoro-1-methylcyclopentene. This was confirmed by chemical means. Although trifluoromethyl groups on non-vinylic carbon atoms are stable, those on vinylic carbon atoms can readily be hydrolysed to carboxyl groups.[7] Thus decafluoro-1-methylcyclopentene was hydrolysed by potassium hydroxide to give heptafluorocyclopentene-1-carboxylic acid. Decafluoro-1-methylcyclopentene was oxidized with potassium permanganate to the anticipated hexafluoroglutaric acid.

A mixture of the two perfluorocyclopentenes, which constituted the major reaction product, was chlorinated and the mixture of products was separated by preparative gas chromatography to give *cis*- and *trans*-1,2-dichloro-octafluorocyclopentanes, and a mixture of *cis*- and *trans*-1,2-dichlorodecafluoro-1-methylcyclopentanes. A similar mixture of the two olefines was fluorinated over cobaltic fluoride, and the products were shown to be decafluorocyclopentane and dodecafluoromethylcyclopentane. The identity of the last compound was established by comparison with authentic material prepared by the fluorination of methylcyclopentane over cobaltic fluoride.

The use of steel Dixon gauzes in place of nickel gauze in the pyrolysis of perfluorodicyclohexylmethane gave a similar pattern of products, although small amounts of hexafluorobenzene and octafluorobenzene and octafluorotoluene were also formed.

Perfluoro-1,2-dicyclohexylethane decomposed over heated nickel gauzes only at temperatures above 600°. The major product of the pyrolysis was the mixture of the cyclopentenes described above. This was verified by chlorination of the mixture and separation of the products in the manner used before. A minor group of reaction products appeared on mass spectrometric examination to be a mixture of decafluorocyclohexene, a tetradecafluoroethylcyclohexene, and a dodecafluoromethylcyclohexene. Passage of perfluoro-1,4-dicyclohexylbutane over heated nickel gauzes at temperatures above 600° also gave predominantly the mixture of cyclopentenes already described.

Perfluoroisopropylcyclohexane reacted with heated nickel gauze, at temperatures above 600°, to give a mixture containing perfluoro-α-methylstyrene and hexafluorobenzene. These products were obtained only in small yields, and the major reaction products were the fluorinated cyclopentenes obtained in the pyrolyses of the other compounds mentioned.

The failure of these attempted defluorination reactions is clearly due to the intervention of a competing thermal reaction in the pyrolysis tube. Thermal reactions of perfluoroisopropylcyclohexane have been studied previously in this Department.[8] Passage of this compound together with chlorine, bromine, or toluene, through a heated tube packed with glass chips, yielded respectively chloro-, bromo- and H-undecafluorocyclohexanes. Similar cleavage of perfluoromethylcyclohexane does not take place, and the preferential cleavage of the tertiary carbon–carbon bond has been demonstrated by the pyrolysis of perfluoro-1-methyl-4-isopropylcyclohexane in the presence of chlorine, bromine, or toluene, to give respectively 1-chloro-, 1-bromo- and 1H-4-trifluoromethyldecafluorocyclohexanes.[9] These reactions were thought to, involve the formation of the appropriate perfluorocyclohexyl radicals. In order to

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[7] W. K. R. Musgrave, *Quart. Revs.* **8**, 331 (1954).

[8] G. B. Barlow and J. C. Tatlow, *J. Chem. Soc.* 4695 (1952).

[9] G. B. Barlow, M. Stacey and J. C. Tatlow, *J. Chem. Soc.* 1749 (1955).

study the reactions of these radicals and to verify their supposed formation, perfluoroisopropylcyclohexane was pyrolysed in tubes packed with glass chips in the absence of any other reactant. At temperatures below 400° only unchanged starting material was recovered, but at temperatures above 420° (using the same conditions of flow through the pyrolysis tube) a mixture of products was obtained containing little or no starting material.

The product obtained at higher temperatures was shown by gas chromatography to contain two components. The first of these was a saturated compound, and mass spectrometry suggested that it had the molecular formula C_6F_{12}. The compound was neither dodecafluorocyclohexane nor dodecafluoromethylcyclopentane, and appeared to be a dodecafluorodimethylcyclobutane. It was most probably formed from the heptafluoroisopropyl radical or some compound derived from this portion of the perfluoroisopropylcyclohexane molecule since it was not found among the products of the pyrolysis of perfluorocyclohexylmethane under similar conditions. Dodecafluorodimethylcyclobutanes are obtained by the action of heat on hexafluoropropene,[10] which could be formed in the present reaction system by the loss of a fluorine atom from the heptafluoropropyl radical. No perfluoro-2,3-dimethylbutane, which might be formed by dimerization of heptafluoropropyl radicals, was found among the pyrolysis products. The second product of the pyrolysis of perfluoroisopropylcyclohexane was a mixture of octafluorocyclopentene and decafluoro-1-methylcyclopentene. Chlorination of this mixture showed that octafluorocyclopentene was present in excess.

The decomposition of the compounds studied, which competes with their defluorination over heated metal surfaces, and which also takes place in glass tubes, would seem to involve the formation of undecafluorocyclohexyl radicals. Loss of fluorine could then occur with the formation of decafluorocyclohexene. The radical can also isomerize to give the undecafluoro-2-methylcyclopentyl radical, which gives perfluoromethylcyclopentene by loss of fluorine, or alternatively it can lose a trifluoromethyl radical to form octafluorocyclopentene. The presence of a reactant such as bromine or toluene, as in the experiments of Barlow and Tatlow, makes possible a reaction of the undecafluorocyclohexyl radical before it is able either to isomerize or decompose. The carrying out of the pyrolysis in the presence of different surfaces influences the relative extents of the alternative reactions indicating that the reactions are, in part at least, heterogeneous. Although it is not suggested that the mechanisms of the process are similar, since the case to be cited is almost certainly homogeneous, it is noteworthy that cyclohexyl radicals, produced by the reaction of methyl radicals with cyclohexane,[11] or by the mercury-photosensitized decomposition of cyclohexane,[12] have been shown to isomerize to give methylcyclopentyl radicals at temperatures of about 400°, and a major end product is methylcyclopentane formed in abstraction regions.

The compounds studied differ in their pyrolytic behaviour from a wide range of other perfluorocyclohexanes that have been successfully defluorinated by pyrolysis over iron. Although their conversion to related aromatic compounds is incomplete, perfluoromethyl-,[1] perfluoroethyl-[1] and perfluorobutyl-[13] cyclohexanes have been

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[10] M. Hauptschein, A. H. Fainberg and M. Braid, *J. Amer. Chem. Soc.* **80**, 842 (1958).

[11] A. S. Gordon and S. R. Smith, *J. Phys. Chem.* **66**, 521 (1962).

[12] S. Arai, S. Sato and S. Shida, *J. Chem. Phys.* **33**, 1277 (1960).

[13] P. L. Coe, J. C. Tatlow and A. Whittingham, unpublished work.

defluorinated, and no evidence of breakdown products of the type noted above has been observed. Perfluorodicyclohexyl has also been defluorinated without evidence of extensive breakdown to simpler materials.[1] The cleavage of the bond between the isopropyl and cyclohexyl fragments in perfluoroisopropylcyclohexane can be understood in terms of the bond's being weakened by steric factors on account of its involving two tertiary carbon atoms. However, this compound did undergo some defluorination. It is difficult to account for the complete pyrolytic breakdown of the other compounds with the exclusion of defluorination, and to understand, for instance, the difference in behaviour between perfluorodicyclohexylbutane and perfluorobutylcyclohexane.

When defluorinated over iron, perfluoroisopropylcyclohexane gave, in addition to the cyclopentyl compounds, small amounts of hexafluorobenzene and of a new compound shown by mass spectrometry, by its analysis, and by its IR spectrum to be decafluoro-α-methylstyrene. An interesting feature of the UV spectrum of this compound ($\varepsilon_{\max} = 1700$ at 245 mμ) was its difference from that of octafluorostyrene[14] ($\varepsilon_{\max} = 5700$ at 235 mμ). The trifluoromethyl substituent on the double bond appears therefore to have shifted the absorption towards the visible region and to have reduced the extinction coefficient. The oxidation of decafluoro-α-methylstyrene with potassium permanganate failed to yield any anticipated product such as octafluoroacetophenone, or pentafluorobenzoic acid.

EXPERIMENTAL

Perfluorocarbons used in the pyrolyses were prepared as described in previous papers,[8,15] with the exception that perfluoro-1,4-dicyclohexylbutane was made from 1,4-diphenylbut-3-ene instead of from 1,4-diphenylbuta-1,3-diene. The desired products were isolated by distillation and preparative gas chromatography.

Pyrolysis of perfluorodicyclohexylmethane

Over nickel gauze. Perfluorodicyclohexylmethane (4·5 g) was passed in a stream of nitrogen (10 l./hr) over Ni gauze contained in a Ni tube (1″ diam, 2′6″ long), the central portion (about 10″) of which was contained in a furnace. The products (3·7 g) of a typical run made at 750° were collected in a trap immersed in liquid air. The more volatile portion of these (0·5 g) showed an IR spectrum identical with that of hexafluoroethane. The remaining components were separated by preparative gas chromatography (using dinonyl phthalate as stationary phase) to give a mixture of decafluoromethyl- and octafluoro-cyclopentenes (2·1 g), as described below, and decafluorocyclohexane (0·05 g). Pyrolyses were carried out at other temps, but using this flow rate only starting material was recovered at temps below 550°.

Over steel Dixon gauzes. These experiments were made using the same apparatus, packed instead with steel Dixon gauzes. Perfluorodicyclohexylmethane (2·9 g) gave at 550° a mixture of products (1·5 g). The combined products (8·1 g) of several similar reactions were separated as above by gas chromatography to give a mixture of decafluoromethyl- and octafluoro-cyclopentenes (4·6 g), decafluorocyclohexene (0·1 g), hexafluorobenzene (a trace) and octafluorotoluene (0·1 g).

The identities of known compounds in these and other experiments were, unless otherwise stated, verified by IR spectroscopy.

Study of mixtures of decafluoromethyl- and octafluoro-cyclopentenes

Gas chromatography. The mixtures such as those obtained in the above experiments were separated by gas chromatography using perfluorodicyclohexylethane (on Kieselguhr) as stationary phase at

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[14] B. R. Letchford, C. R. Patrick, M. Stacey and J. C. Tatlow, *Chem. & Ind.* 1472 (1962).

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

room temp, to give only octafluorocyclopentene, and *decafluoromethylcyclopentene* (mass spectrometry principal mass peaks: 262 (C_6F_{10}), 243 (C_6F_9), 212 (C_5F_8) and 193 (C_5F_7). The IR spectrum showed a strong band at 1725 cm^{-1}).

Chlorination. A mixture of the cyclopentenes (3·5 g; obtained by the pyrolysis of perfluoro-1,2-dicyclohexylethane) and chlorine (1·2 g) was irradiated (using a Hanovia SP 250 lamp) in a sealed tube for 6 days. The product (3·0 g) was washed ($Na_2S_2O_5$ aq and with water), dried and separated by preparative gas chromatography (using dinonyl phthalate as stationary phase) to give *cis*- and *trans*-1,2-dichlorooctafluorocyclopentane (0·65 g), identified by comparison with authentic specimens, and 1,2-*dichlorodecafluoromethylcyclopentane* (1·3 g) m.p. 61° (Found: C, 21·5; Cl, 21·0; $C_6F_{10}Cl_2$ requires: C, 21·6; Cl, 21·3%). Mass spectrometry: principal mass peaks 334 and 332 ($C_6F_{10}Cl_2$). In a similar way the appropriate mixtures from other pyrolyses were chlorinated, and the chloro compounds separated by gas chromatography. Thus a portion (4·0 g) of chloro compounds from the products of pyrolysis of perfluorodicyclohexylmethane over Ni gave 1,2-dichlorooctafluorocyclopentane (0·3 g) and 1,2-dichlorodecafluoromethylcyclopentane (1·9 g). The chloro compounds derived from the products of defluorination of perfluoroisopropylcyclohexane over glass (2·9 g) gave 1,2-dichlorooctafluorocyclopentane (0·6 g) and 1,2-dichlorodecafluoromethylcyclopentane (0·4 g).

Fluorination. A mixture of the cyclopentenes obtained from the pyrolysis of dicyclohexylmethane over Ni (9·7 g) was vaporized into a static cobaltic fluoride reactor[16] heated to 190°. The product (7·5 g) was collected in a copper trap, cooled in solid carbon dioxide. Of this, a portion (3·2 g) was separated by preparative gas chromatography (using dinonyl phthalate as stationary phase) to give decafluorocyclopentane (0·3 g) and *dodecafluoromethylcyclopentane* (1·5 g) b.p. 49·5°. (Found: C, 23·7; C_6F_{12} requires: C, 24·0%). Mass spectrometry: principal mass peaks: 281 (C_6F_{11}), 262 (C_6F_{10}), 243 (C_6F_9) and 231 (C_5F_9). This compound was identical with the principal product of the fluorination of methylcyclopentane in the same reactor.

Hydrolysis. A mixture of the cyclopentenes (6·0 g), KOH (6·0 g), and water (8 ml) was heated under reflux for 3 hr. The aqueous layer was separated from the unreacted fluorocarbon layer (1·4 g) and extracted with ether (3 × 30 ml). After acidification with H_2SO_4 the aqueous layer was extracted with ether continuously overnight. The dried ($MgSO_4$) ether extract was evaporated leaving a brown residue (2·3 g). A portion (0·8 g) of this was dissolved in water and treated with S-benzylthiouronium chloride to give a precipitate (1·0 g). Recrystallization of this from aqueous ethanol gave *S-benzylthiouronium heptafluorocyclopentene*-1-*carboxylate* (0·7 g) m.p. 185° (Found: C, 41·6; H, 2·5. $C_{14}H_{11}F_7N_2SO_2$ requires: C, 41·6; H, 2·7%).

Oxidation. A mixture of the cyclopentenes (1·0 g) was oxidized with $KMnO_4$ (3·0 g) in acetone (250 ml). The product was precipitated by the addition of freshly distilled aniline. Recrystallization of the precipitate from acetone–chloroform gave dianilinium hexafluoroglutarate (0·63 g) m.p. 219°, (lit.[8] 219–221°).

Decafluoro-α-methylstyrene by the pyrolysis of perfluoroisopropylcyclohexane

Perfluoroisopropylcyclohexane (3·6 g) was passed in a stream of N_2 (1·5 l./hr) over Ni gauzes contained in the pyrolysis apparatus described before which was maintained at 750°. The products (0·8 g) were collected in a trap immersed in liquid air. The accumulated product of several similar runs (19 g) were separated by preparative chromatography to give a mixture of octafluorocyclopentene, decafluoromethylcyclopentene and decafluorocyclohexane (9·1 g), and *decafluoro-α-methylstyrene* (1·3 g) b.p. 128° (Found: C, 35·9; F, 63·6; C_9F_{10} requires C, 36·3; F, 63·7%). Mass spectrometry: principal mass peaks (298 (C_9F_{10}), 279 (C_9F_9) and 267 (C_8F_9). The UV spectrum showed a single peak in the region above 220 mμ, (λ_{max} 245 mμ, $\varepsilon_{max} = 1700$).

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[16] D. E. M. Evans, J. A. Godsell, R. Stephens, J. C. Tatlow and E. H. Wiseman, *Tetrahedron* **2**, 183 (1958).