418. *Polyfluoroarenes. Part III.*[1] *A New Synthesis of Hexafluorobenzene.*

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Pyrolysis of 1-chloro-1,2-difluoroethylene over a platinum surface at 600° gave hexafluorobenzene in 14% yield. Hexafluorobenzene was not produced by pyrolysis of 1,2-dichlorodifluoroethylene under a variety of conditions, but low yields were obtained by co-pyrolysis with hydrogen.

In Part I of this series [2] it was suggested that the formation of hexafluorobenzene during the pyrolysis of tribromofluoromethane involved difluoroacetylene as an intermediate:

$$CFBr_3 \longrightarrow CFBr_2{\cdot}CFBr_2 \longrightarrow C_2F_2 \longrightarrow C_6F_6$$

This view led to an investigation of the pyrolysis of a number of 1,2-difluoroethylenes which might, by thermal dehalogenation or dehydrohalogenation, yield difluoroacetylene and hence hexafluorobenzene. The results of studies of the pyrolysis of 1,2-dichlorodifluoroethylene and 1-chloro-1,2-difluoroethylene are now reported.

1,2-Dichlorodifluoroethylene was prepared from a mixture of tetrachlorodifluoroethanes containing 60—90% of the symmetrical isomer. This mixture could not be separated by distillation ($CF_2Cl{\cdot}CCl_3$, b. p. [3] 92·8°; $CFCl_2{\cdot}CFCl_2$, b. p. [3] 91·5°) or by gas-liquid chromatography, but dechlorination with zinc in ethanol gave the related dichlorodifluoroethylenes in excellent yield (>90%). Separation of the mixture of olefins by distillation was not attempted ($CF_2{:}CCl_2$, b. p. [4] 19°; *cis*-$CFCl{:}CFCl$, b. p. [3] 21·1°; *trans*-$CFCl{:}CFCl$, b. p. [3] 22°), but the mixture was analysed by gas–liquid chromatography and the symmetrical olefin was isolated by utilising the preferential reaction of 1,1-dichlorodifluoroethylene with ethoxide ion. The mixture of olefins was treated under mild conditions with an excess of ethanol containing a trace of sodium ethoxide. 1,1-Dichlorodifluoroethylene added ethanol and remained in solution,[5] and 1,2-dichlorodifluoroethylene was removed by distillation. The latter olefin undergoes base-catalysed addition of ethanol only under more vigorous conditions.[6]

Photochemical reaction of hydrogen bromide with 1,2-dichlorodifluoroethylene, followed by dehalogenation of the adduct, gave 1-chloro-1,2-difluoroethylene in 87% overall yield.

1-Chloro-1,2-difluoroethylene was pyrolysed by passage under atmospheric pressure through a platinum tube at 590—650° and contact-times of 0·4 to 2·3 min. Hexafluorobenzene was readily detected in the complex mixture of products by its characteristic infrared absorption at 1536 cm.$^{-1}$,[2] and the yield was determined by gas–liquid chromatographic analysis. The best yield (14%) of hexafluorobenzene was obtained with a

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[1] Part II, Birchall and Haszeldine, *J.*, 1959, 3653.
[2] Birchall and Haszeldine, *J.*, 1959, 13.
[3] Locke, Brode, and Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726.
[4] Henne and Wiest, *J. Amer. Chem. Soc.*, 1940, **62**, 2051.
[5] Tarrant and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 1781.
[6] Ruh, U.S.P. 2,737,530/1956; *Chem. Abs.*, 1956, **50**, 10758g.

contact-time of 2·3 min. at a furnace temperature of 600°. Attempts to separate hexafluorobenzene from the products of pyrolysis by distillation were unsuccessful with the quantities used, but the pure compound was obtained by preparative-scale gas–liquid chromatography. Pyrolysis of 1-chloro-1,2-difluoroethylene over a nickel surface at 600—750° gave lower yields (1—2%) of hexafluorobenzene.

1,2-Dichlorodifluoroethylene was pyrolysed over nickel and over iron surfaces, in an atmosphere of nitrogen at temperatures of 450—1000°, but no hexafluorobenzene was produced. Under conditions leading to the elimination of chlorine, extensive carbonisation occurred and an intractable mixture of products was obtained. However, one experiment in which 1,2-dichlorodifluoroethylene was pyrolysed in the presence of hydrogen, in a platinum tube at 625°, gave hexafluorobenzene in *ca.* 2% yield.

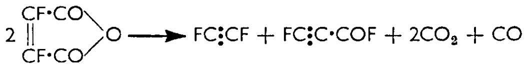
It is emphasised that no attempts were made to examine all the reaction variables in the above pyrolyses, and it is clear that the yields reported could very probably be raised considerably.

The postulated formation of difluoroacetylene during the pyrolysis of chloro-1,2-difluoroethylene

$$\mathrm{CFCl{:}CFH} \xrightarrow{-\mathrm{HCl}} [\mathrm{C_2F_2}] \longrightarrow \mathrm{C_6F_6}$$

is supported by the observation that pyrolysis of trichloroethylene gives a quantitative yield of hexachlorobenzene; kinetic studies suggest that dichloroacetylene is an intermediate in this reaction.[7]

Difluoroacetylene has recently been reported as a product of the pyrolysis of difluoromaleic anhydride:[8]



Isolation and characterisation of the difluoroacetylene was not achieved, and identification rests on mass-spectrographic analysis. The very limited studies so far reported on difluoroacetylene suggest that it decomposes vigorously with extensive carbonisation, even at low temperatures. The only product mentioned is an unknown structure C_4F_4, and it is not clear whether the possibility of the formation of hexafluorobenzene was considered. It is not known whether the decomposition of difluoroacetylene was spontaneous or induced by the presence of impurity.

On the other hand, monofluoroacetylene, prepared by pyrolysis of monofluoromaleic anhydride, is reported to trimerise spontaneously in the vapour phase to give a low yield of 1,2,4-trifluorobenzene, apparently without the formation of 1,3,5-trifluorobenzene.[9]

EXPERIMENTAL

All chromatography columns to which specific reference is made were packed with 30% w./w. of " dinonyl " phthalate on Celite.

Preparation of 1,2-*Dichlorodifluoroethylene*.—A sample of tetrachlorodifluoroethane (500 g.) in ethanol (150 ml.) was added during 2 hr. to a stirred suspension of activated zinc dust (1250 g.) in ethanol (800 ml.) at 30—40°. The volatile products were distilled continuously from the reactants and collected in traps cooled to −78°. The mixture was later heated under gentle reflux to ensure complete removal of the products. Redistillation gave dichlorodifluoroethylene (300 g.; 92%), b. p. 19—20·5° (Found: *M*, 134. Calc. for $C_2Cl_2F_2$: *M*, 133), shown by gas–liquid chromatography (2-m. column at room temperature) to contain 1,2-dichlorodifluoroethylene (64%) and 1,1-dichlorodifluoroethylene (36%).

A solution from sodium (6·0 g.) and ethanol (100 ml.) was added cautiously at room temperature to the dichlorodifluoroethylene mixture (300 g.) dissolved in ethanol (500 ml.). After a

[7] Goodall and Howlett, *J.*, 1954, 2599.
[8] Middleton, U.S.P. 2,831,835/1958; *Chem. Abs.*, 1958, **52**, 14658f.
[9] Middleton and Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 803.

short induction period, a vigorous reaction commenced and continued for 15 min. The mixture was heated under reflux for 3 hr. and the volatile product was then distilled, dried (P_4O_{10}), and redistilled to give 1,2-dichlorodifluoroethylene (186 g.), b. p. 20° (Found: C, 18·3%; *M*, 133. Calc. for $C_2Cl_2F_2$: C, 18·1%; *M*, 133), identified by infrared spectroscopy. Chromatographic analysis (4-m. column at room temperature) indicated the presence of only one component.

*Preparation of Chloro-*1,2-*difluoroethylene.*—1,2-Dichlorodifluoroethylene (50 g.; 0·38 mole) and hydrogen bromide (31 g.; 0·38 mole), in a 20-l. " Pyrex " bulb, were irradiated by a 500-w mercury discharge tube, inserted into a silica tube in the centre of the bulb. The reaction, which was followed by pressure readings, was complete after 1 hr. Distillation gave 1-*bromo*-1,2-*dichloro*-1,2-*difluoroethane* (75 g.; 93%) (Found: C, 11·4; H, 0·5%; *M*, 215. $C_2HBrCl_2F_2$ requires C, 11·5; H, 0·5%; *M*, 214), b. p. 98°, n_D^{20} 1·4307.

The bromo-compound was added gradually to a stirred suspension of activated zinc dust (160 g.) in ethanol (110 ml.) at 30—40°. At the end of the reaction, water was added and the product was distilled, dried (P_4O_{10}), and redistilled to give 1-chloro-1,2-difluoroethylene (31 g.; 94%) (Found: C, 24·7; H, 1·0%; *M*, 99. Calc. for C_2HClF_2: C, 24·4; H, 1·0%; *M*, 98·5), b. p. −15° (Ruh and Rector [10] give b. p. −16° to −14·5°/744 mm.). The product was shown to be a *cis-trans* mixture by gas–liquid chromatography (resolved easily on a 4-m. column at room temperature). It showed C=C stretching absorption at 1709 and 1721 cm.$^{-1}$ (doublet).

*Pyrolysis of Chloro-*1,2-*difluoroethylene.*—The apparatus for pyrolysis over platinum was essentially that described earlier for the pyrolysis of tribromofluoromethane.[2] 1-Chloro-1,2-difluoroethylene vapour was introduced in a slow stream of nitrogen (100 ml./hr.), and the products were collected in traps at −78° and −196°. Under the best conditions found, the olefin (94·0 g.) was introduced into the platinum tube at a constant rate of 6·5 g./hr. (contact-time, 2·3 min.) with a furnace temperature of 600°. Hydrogen chloride (14·7 g.; 42%) and unreacted chloro-1,2-difluoroethylene (35·6 g.; 38%) were removed by distillation. The remaining material was shown by infrared spectroscopy and gas–liquid chromatography to contain hexafluorobenzene (5·3 g.; 9%; 14% on olefin transformed) and several other components. Gas–liquid chromatographic equipment was carefully calibrated with a pure sample of hexafluorobenzene.[2] Distillation of the products followed by preparative-scale gas–liquid chromatography (3-m. column) gave hexafluorobenzene (3·8 g.) (Found: C, 38·6%; *M*, 183. Calc. for C_6F_6: C, 38·7%; *M*, 186), identified by infrared spectroscopy.

This result is compared with those of other experiments in the Table.

Temp.	590°	600°	620°	620°	650°
C_2HClF_2 (g./hr.)	6·5	6·5	6·5	13·0	32·5
C_2HClF_2, % recovered	44	38	29	45	65
C_6F_6, % net yield	11	14	8·5	6	5

Pyrolysis of 1-chloro-1,2-difluoroethylene over nickel was carried out similarly, a nickel tube of 18 mm. i.d. being used, heated over 40 cm. of its length in an electric furnace. Pyrolysis of the olefin at 650° with a flow rate of 27 g./hr. in a slow stream of nitrogen (100 ml./hr.) gave a 1—2% yield of hexafluorobenzene. Lower yields were obtained from experiments at other furnace temperatures and flow rates.

Pyrolysis of 1,2-*Dichlorodifluoroethylene.*—(a) *In nitrogen.* 1,2-Dichlorodifluoroethylene was similarly pyrolysed in the nickel tube, at 600—1000° and flow rates of 10—100 g./hr. Spectroscopic and chromatographic analysis of the products showed that no hexafluorobenzene was produced.

Pyrolysis at 450° and 550° in the nickel tube packed with clean iron gauze also failed to yield hexafluorobenzene.

(b) *In hydrogen.* 1,2-Dichlorodifluoroethylene (10·0 g./hr.) was pyrolysed in a stream of hydrogen (2·14 l./hr.) in the platinum tube at 625°. After a preliminary distillation, the product was shown by infrared spectroscopy and gas–liquid chromatography to contain hexafluorobenzene (*ca.* 2%).

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[10] Ruh and Rector, U.S.P. 2,716,109/1956.