[CORNELL UNIVERSITY AND THE S. A. M. LABORATORIES OF THE MANHATTAN PROJECT, ITHACA, N. Y., AND COLUMBIA UNIVERSITY, NEW YORK, N. Y.]

The Thermal Polymerization of Hexafluorobutadiene[1]

BY MAURICE PROBER[2] AND WILLIAM T. MILLER, JR.

The unsaturated fluorocarbons have been of especial interest in this Laboratory because of their high order of reactivity, and consequent suitability for study and for use as synthetic intermediates, in marked contrast to corresponding chloro compounds. Hexafluoro-1,3-butadiene, the first fluorocarbon diolefin prepared[3] and investigated, was found to exhibit a chemical reactivity in many ways rivaling its hydrogen analog. It underwent radical chain type and thermal polymerization and was readily halogenated and attacked by neutral permanganate in contrast to the comparatively inert hexachloro-1,3-butadiene.[4] The present paper reports on the thermal reactions of hexafluoro-1,3-butadiene and of its dimer and trimer.

The thermal polymerization of conjugated hydrocarbons has already been studied in the case of a number of dienes.[5-17] At elevated temperatures there was appreciable formation of dimers and in some cases trimers. High molecular weight products were also formed in the liquid phase thermal reactions unless special precautions were taken to remove peroxides and oxygen. Dimerization may be generally represented by 1,4-addition of one molecule of a diene to a double bond of a second molecule and the dimers of butadiene, isoprene and 2,3-dimethylbutadiene, and the trimer of butadiene all have been reported to have cyclohexene structures.[5,8,12,15,18] However, 1-phenyl-1,3-butadiene appears to be an exceptional case and a cyclopentene structure has been assigned to its thermal dimer.[17,18a] Kinetic studies of vapor phase thermal diene dimerizations have indicated a homogeneous second order reaction.[6,7,9]

Thermal Reactions of Hexafluorobutadiene.—On the basis of preliminary work, the thermal reactions of hexafluoro-1,3-butadiene have now been investigated over the temperature range of 150 to 180°. The reactions were carried out by heating the diene in steel bombs with not more than trace amounts of water or oxygen normally present. The reaction products were hexafluorocyclobutene, dimers which distilled at 98 to 100°, trimers which distilled at 64 to 66° at 10 mm., and some higher boiling material. The higher boiling fractions were viscous liquids which indicated that the degree of polymerization was low. In the higher temperature runs small amounts of a compound boiling below the dimer fraction but with the empirical formula C_8F_{12} was isolated as well. The reaction product was readily separated into its major components, which differed by four carbon units, by fractional distillation. The recovered butadiene fraction was analyzed by chlorination and separation of the resulting dichloride and tetrachloride by fractional distillation. Experimental data are summarized in Table I.

These data indicated that the yields of the different products were strongly influenced by reaction temperature. Similar observations have been made for the thermal dimerization of butadiene,[10] but a comparison of the reactivity of the two dienes is complicated by the side reactions in the case of hexafluorobutadiene to form cyclobutene and trimer. Intramolecular cyclization became more pronounced as the reaction temperature was increased, and at 500° and atmospheric pressure, hexafluorobutadiene was quantitatively converted to hexafluorocyclobutene when passed through a heated tube with a five to fifteen second contact time.[19] Under comparable conditions, butadiene undergoes dimerization.[20] Although a trimer has been obtained by heating vinylcyclohexene and butadiene, the yield was very poor.[18] Formation of a trimer proceeded more rapidly with hexafluorobutadiene, and as shown above this fraction constituted a considerable portion of the reaction product. As might be expected

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[2] Present address: General Electric Company, Schenectady, N. Y.

[3] Miller, Ehrenfeld, Phelan, Prober and Reed, *Ind. Eng. Chem.*, **39**, 401 (1947).

[4] Fruhwirth, *Ber.*, **74**, 1700 (1941).

[5] Lebedev, *Bull. soc. chim.*, **12**, 780 (1912).

[6] Vaughan, This Journal, **54**, 3863 (1932).

[7] Harkness, Mears and Kistiakowsky, *J. Chem. Phys.*, **5**, 682 (1937).

[8] Lebedev and Sergjenko, *Chem. Zentr.*, **107**, II, 59 (1936).

[9] Kistiakowsky and Ransom, *J. Chem. Phys.*, **7**, 725 (1939).

[10] Robey, Wiese and Morrell, *Ind. Eng. Chem.*, **36**, 3 (1944).

[11] Wallach, *Ber.*, **24**, 1538 (1891).

[12] Lebedev and Skavronskai, *Bull. soc. chim.*, **16**, 82 (1914).

[13] Whitby and Crozier, *Can. J. Res.*, **6**, 203 (1932).

[14] Aschan, *Ann.*, **461**, 9 (1928).

[15] Wagner-Jauregg, *ibid.*, **488**, 178 (1931).

[16] Whitby and Gallay, *Can. J. Res.*, **6**, 280 (1932).

[17] Bergmann, *J. Chem. Soc.*, 1359 (1935).

[18] Alder and Rickert, *Ber.*, **71**, 373 (1938).

[18a] Since this paper was prepared, Foster and Schreiber, This Journal, **70**, 2303 (1948), have described the preparation of cyclooctadienes from 2-chloro-1,3-butadiene, in moderate yield, and from 1,3-butadiene and 2,3-dichloro-1,3-butadiene, in small yields, and have drawn our attention to the isolation of an 8-carbon ring dimer from chloroprene still residues by Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

[19] F. H. Winslow and W. T. Miller, Jr., unpublished work.

[20] Moor, Strigaleva and Shilyaeva, *C. A.*, **30**, 365 (1936).

TABLE I

THERMAL POLYMERIZATION OF HEXAFLUOROBUTADIENE

No.	Reaction conditions Time, hr.	Reaction conditions Temp., °C.	Conversion,[a] %	Products[b] Cyclobutene C_4F_6	Products[b] Low b. p. C_8F_{12}	Products[b] Dimer C_8F_{12}	Products[b] Trimer $C_{12}F_{18}$	Products[b] High b. p. residue
1[c]	44	150	83	6.4	0	67	19	1.5
2[d]	44	150	79	6.7	0	67	15	1.1
3[c,e]	44	150	77	6.9	0	65	18	1.9
4[f]	5	160	39	5.3	0	88	3.6	0.2
5[d,f]	5	160	37	5.6	0	89	3.2	0.5
6[d,f]	18	180	94	14	2.0	40	30	3.9
7[d,f]	18	180	94	14	2.5	38	33	4.1
8[d,f]	44	180	99[g]	14	5.1	33	34	6.0

[a] Conversions are calculated on the basis of all reaction products recovered including intermediate fractions. [b] Yields expressed as weight per cent. of hexafluorobutadiene converted. [c] Charged under nitrogen. [d] Charged under air. [e] Catechol, 0.3 g., added. [f] Dissolved gases removed by distillation. [g] Complete reaction; the conversion is less than 100% because of losses in handling.

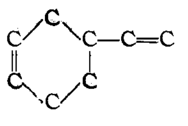
on the basis of a stepwise reaction mechanism, heating hexafluorobutadiene with excess dimer yielded considerably more trimer than was obtained directly.

The presence of oxygen or an anti-oxidant such as catechol did not affect the composition of the products as shown in Table I by the results of reactions 1, 2 and 3 further supporting a molecular type thermal reaction and in all cases the residues were indicated as very low polymers. These results differ considerably from those observed with the hydrocarbon dienes where the presence of oxygen generally leads to appreciable yields of high polymer.

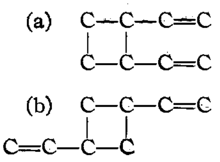
With the exception of hexafluorocyclobutene, the structures of the thermal reaction products of hexafluorobutadiene have not been proved. The lack of related compounds was a major handicap to this work. However, some progress was made toward assigning structures to the dimer products. Analyses and molecular weight determinations confirmed the molecular formula, C_8F_{12}, and the presence of more than one isomer was indicated by the absence of a sharp boiling point and failure to obtain a plateau in the cooling curve. Chlorination confirmed this conclusion, and yielded tetrachloride, and hexachloride in approximately 2.5 to 1 molar ratio. Both chlorides were saturated to permanganate in acetone. The presence of structural isomeric chlorides was not excluded.

The dimer skeletons derivable from hexafluorobutadiene without carbon–carbon or carbon–fluorine bond rearrangements, which are capable of yielding tetrachlorides are listed below.

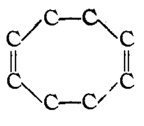
I



II



III



Little direct evidence was available to indicate a preferred structure. All of the hydrocarbon dimers formed from dienes which have been examined[5,8,13,14,15] with the exception of the dimer from 1-phenylbutadiene[17] have been indicated as cyclohexene ring compounds. By analogy, hexafluorobutadiene would undergo a similar reaction to form structure I. However, one of the interesting differences between fluorocarbon and hydrocarbon chemistry is the more ready formation of cyclobutane structures with the highly fluorinated systems. Examples are the cyclobutane dimer formed by heating tetrafluoroethylene,[21] chlorotrifluoroethylene,[21,22] or unsym.-dichlorodifluoroethylene,[21,22] and the cyclization of hexafluorobutadiene to hexafluorocyclobutene described above. In addition, the thermal reactions of the dimer fraction could be best explained by assuming a cyclobutane structure for at least one of the isomers.

No data were collected with specific reference to the non-planar cycloöctadiene structure III. It is planned to continue work on the hexafluorobutadiene dimer structures by oxidation. Different acids should be obtained from I, II and III.

The preparation of the hexachloride, $C_8Cl_6F_{12}$, from the dimer fraction indicated the presence of a dimer with a structure formed by rearrangement as well as condensation. Formation of hexachloride by ring cleavage of tetrachloride was unlikely because chlorination at 0 and 100° yielded the same tetrachloride: hexachloride ratios and because of the observed difficulty of cleaving known fluorinated cyclobutane compounds with chlorine.

The absence of a sharp boiling point also indicated the presence of more than one isomeric trimer.

Thermal Reactions of Hexafluorobutadiene Dimers.—When the hexafluorobutadiene dimer fraction was heated in a glass bomb at 200° for one hundred and sixty-four hours, 40% was converted into a remarkable isomeric compound,

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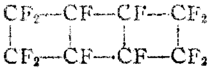
(21) Harmon, U. S. Patent 2,404,374, July 23, 1946.

(22) Henne and Ruh, THIS JOURNAL, 69, 279 (1947). The thermal dimerization of tetrafluoro- and of the chlorofluoroethylenes to form cyclobutanes was also carried out independently by Miller and his associates as a part of the fluorocarbon war research program.

C_8F_{12}, which boiled at 80° and melted at 40°. Reheating the recovered high boiling C_8F_{12} yielded a total conversion for the two cycles of about 65% of the original fraction to the low boiling isomer. The purified low boiling compound was entirely stable to permanganate and to chlorination. Its formula was checked by molecular weight determinations and by analysis. These facts require a fused tricyclic structure such as IV. Such a compound could be formed by

IV


intramolecular condensation of *cis*-dodecafluoro-1,2-divinylcyclobutane, IIa, or dodecafluoro-1,5-cycloöctadiene, III, without rearrangement of groups. Evidence for the ready formation of cyclobutane rings in fluorinated systems has been presented above. The stability of a simple cyclobutane ring was also demonstrated by passing 1,2-dichlorohexafluorocyclobutane and excess chlorine through a heated glass tube. No reaction occurred until pyrolysis temperatures approaching 500° were reached. The relatively high melting point of 40° of the saturated C_8F_{12} suggested a symmetrical structure, but no other direct chemical evidence was available to support the structure postulated for this unusual material. However, preliminary X-ray diffraction studies on the crystalline C_8F_{12} compound by Professor J. L. Hoard and Mr. R. W. Broge of this Laboratory have yielded results which are consistent with the tricyclic structure proposed above.

In addition to the low boiling isomer, a white infusible polymer was isolated in low yield from the bomb reactions of hexafluorobutadiene dimer. This polymer was insoluble in acetone, pentane, ethyl alcohol, carbon tetrachloride, benzene, C_8F_{16}, and 1,1,2-trichlorotrifluoroethane and decomposed on heating above 300°.

A 60% yield of the low boiling saturated C_8F_{12} isomer was obtained by passing the dimer fraction through a hot tube at 500°. The recovered dimer fraction was recycled, but did not yield additional low boiling C_8F_{12}. The recovered material was chlorinated and yielded only tetrachloride, indicating the absence of triene, and it was considered significant that the physical properties of this tetrachloride fraction were not identical with those of the tetrachloride fraction isolated by direct chlorination of hexafluorobutadiene dimer as described above. Approximately five per cent of the dimer fraction underwent depolymerization in the hot tube reaction. The C_4F_6 product isolated was hexafluorocyclobutene which, under the conditions of the experiment would have been formed from hexafluorobutadiene. No products boiling higher than C_8F_{12} were obtained from the hot tube reactions.

Thermal Reactions of the Hexafluorobutadiene Trimer.—The trimer was found to undergo polymerization when heated at 300° in a sealed tube. After one hundred and sixteen hours, approximately 35% $C_{12}F_{18}$ fraction was recovered, 30% boiled from 175 to 200° at 10 mm., probably C_{24} fractions, and the remainder did not distil at a bath temperature of 300° under 1.5 mm. pressure. Less than 5% low boiling material was formed and the recovered $C_{12}F_{18}$ was indicated as approximately equivalent in unsaturation to the starting material by permanganate titration. Partial depolymerization occurred when the trimer was passed through a hot tube at 520°.

Experimental

Hexafluorobutadiene.—Hexafluorobutadiene was prepared by dechlorination of 1,2,3,4-tetrachlorohexafluorobutane. The tetrachloride was gradually added to a hot stirred suspension of zinc dust in absolute alcohol and the diene fractionally distilled out as formed utilizing a partial condenser topped by a short packed column. The product was refluxed over phosphorus pentoxide to remove alcohol and then redistilled through a 70 × 1.2 cm. glass helix packed low temperature column. The fraction b. p. 6.5 to 7.5° (uncor.) was taken for polymerization studies.

Thermal Reactions.—The polymerization bombs were steel "lecture" cylinders[23] in which the conventional valve was replaced by a plug bearing inlet and outlet tubes equipped with brass needle valves. The bombs were thoroughly washed and dried before each run, but the walls were coated with iron oxide. The diene was distilled through a drying tube packed with "Drierite" directly into the bombs under dry oxygen-free nitrogen. The nitrogen was purified by passing it through a series of wash bottles containing Fieser solution,[24] lead acetate solution, and concentrated sulfuric acid, followed by a phosphorus pentoxide tube. In those experiments where the effect of oxygen was tested, a slow stream of dry air was passed through the bomb after it had been charged with diene. The vapor phase was about 200 cc. After the first three experiments this procedure was discarded in favor of charging the bomb under dry air and distilling out 10 to 20 g. of diene to sweep out dissolved gases. The polymerization bombs were heated in a constant temperature oven controlled to ±0.5°, and the reaction times include the time necessary for the bomb to warm up from room temperature. At the conclusion of a run, the bombs were cooled rapidly to room temperature and the contents transferred to a cold still pot under a carbon dioxide atmosphere. It was preferable to carry out the transfer and distillations under an inert atmosphere to avoid oxidation since perfluoro olefins in general undergo ready oxidation to yield acid halide type products in air. The reaction product was distilled through a 75 × 1.0 helix packed column with Dry Ice trap in series. The Dry Ice trap condensate consisted of recovered hexafluorobutadiene and hexafluorocyclobutene, b. p. 0.0°.[25] This mixture was analyzed by chlorination under a Dry Ice reflux condenser with illumination from a quartz mercury vapor lamp. The 1,2-dichlorohexafluorocyclobutane, b. p. 60.4,[26] resulting from the cyclobutene and the 1,2,3,4-tetrachlorohexafluorobutane, b. p. 134.1°,[27] resulting from the diene were readily separated by fractional distillation. The dimer fraction, C_8F_{12}, was collected from 96 to 100° with most of it distilling from 98 to 100°.

Anal. Calcd. for C_8F_{12}: C, 29.56; mol. wt., 324. Found: C, 29.3, 29.6; mol. wt., 326, 331.

In the higher temperature runs, a lower boiling dimer was

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[23] As supplied by the Mathieson Company.

[24] Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 395.

[25] Harmon[21] has reported b. p. 5 to 6°; Henne and Ruh[22] have reported b. p. 1.13°.

[26] Harmon[21] has reported b. p. 58-59°; Henne and Ruh[22] have reported b. p. 59.87°.

[27] Determined by J. M. Phelan

collected over the boiling range 80 to 85°. The behavior of this compound is described below. In the first five runs, the trimer fraction was too small for convenient fractional distillation, and was separated from the higher boiling residue by simple distillation. It was collected over the boiling range 165 to 185° and distilled largely from 175 to 180°. In subsequent runs the residue from the C_8F_{12} distillation was fractionally distilled at 10 mm. and the trimer, $C_{12}F_{18}$, collected, b. p. 62 to 68°, largely b. p. 64 to 66°.

Anal. Calcd. for $C_{12}F_{18}$: C, 29.65. Found: C, 29.7, 29.8.

The quantitative results for the hexafluorobutadiene polymerizations are given in Table I. The amounts of hexafluorobutadiene charged for the eight reactions for which data are given was as follows: Reaction (1), 305 g.; (2), 253 g.; (3), 196 g.; (4), 328 g.; (5), 327 g.; (6), 350 g.; (7), 390 g.; (8), 418 g.

Hexafluorobutadiene Dimer.—The dimer fraction of b. p. 96 to 100°, as indicated above, was utilized for the following experiments.

Chlorination.[28]—Chlorine, 41 g., was passed into 81.7 g. C_8F_{12} while the reaction mixture was illuminated by a mercury vapor lamp. The light source was placed about one foot away to minimize heating effects and the chlorination flask was maintained at 0 to 5° by circulating ice water through a cold finger. The reaction product was washed with 5% sodium hydroxide solution, dried, and fractionally distilled at 20 mm. pressure to yield the following fractions: 6.5 g., Dry Ice-trap condensate; 2.6 g., b. p. 55 to 90.5°; 59.7 g., b. p. 90.5 to 94.0°; 4.3 g., b. p. 94.0 to 138.0°; 27.0 g. b. p. 138.0 to 139.5°; 3.1 g., residue.

The same general procedure as above was carried out with 81.5 g. of C_8F_{12}. However, the liquid was maintained at reflux during the chlorination and varied in temperature from 100° at the beginning to over 200° at the end of the run. The reaction product was washed with 5% sodium hydroxide solution, dried, and refractionally distilled at 20 mm. pressure to yield the following fractions: 7.1 g. Dry Ice-trap condensate; 4.9 g., b. p. 91 to 94°; 68.0 g., b. p. 94 to 127° but principally at 94 to 97°; 1.7 g., b. p. 127 to 138°; 25.8 g., b. p. 138 to 140°.

A heart cut from redistillation of the combined fractions of b. p. 90 to 97° at 20 mm. was found to be saturated to potassium permanganate in acetone; b. p. 203°, 90.5 to 91.5° at 20 mm., $n^{20}D$, 1.3870.

Anal. Calcd. for $C_8Cl_4F_{12}$: C, 20.62. Found: C, 20.6, 20.7.

A heart cut from redistillation of the fraction of b. p. 138 to 140° at 20 mm. was also saturated to permanganate in acetone; b. p. 261°, 139 to 140° at 20 mm.; $n^{20}D$ 1.4040.

Anal. Calcd. for $C_8Cl_6F_{12}$: C, 17.88; Cl, 39.63. Found: C, 18.0, 18.1; Cl, 39.6, 39.3.

The molar ratio of tetrachloride to hexachloride was estimated as 2.5 to 1.0 for the low temperature reaction and 2.8 to 1.0 for the high temperature chlorination; agreement within experimental error.

Thermal Reactions.—Hexafluorobutadiene and its unsaturated dimer, C_8F_{12}, reacted as follows.[29] A steel bomb was charged with 40 g. of C_8F_{12} and 10 g. C_4F_6 and heated for twelve hours at 170°. No unreacted hexafluorobutadiene remained, and 39.8 g. of C_8F_{12} and 7.5 g. of $C_{12}F_{18}$ were obtained. The yield of $C_{12}F_{18}$ was considerably higher than that derived solely from C_4F_6 under comparable conditions and indicated that formation of $C_{12}F_{18}$ proceeded through interaction of C_8F_{12} and C_4F_6.

The unsaturated dimer of hexafluorobutadiene was partially converted by heating into an isomeric saturated compound.

A sealed glass bomb tube containing 56.7 g. of C_8F_{12}, b. p. 96 to 100° was heated at 200° for one hundred and sixty-four hours. The volatile reaction products were distilled out of the bomb to leave 2 g. of white solid residue. Upon slow heating the solid began to darken at 300° and underwent slow decomposition at 400° without melting. The solid was insoluble in acetone, pentane, ethyl alcohol, carbon tetrachloride, C_8F_{16} (satd.), 1,1,2-trichlorotrifluoroethane and benzene. The liquid product was separated into the following fractions by distillation through a small Vigreux column: 19.0 g., b. p. 82 to 86° (solid at room temperature); 6.7 g., b. p. 86 to 96°; 15.3 g., b. p. 96 to 100°; 3.7 g. residue. The 98 to 100° portion of the recovered C_8F_{12} was reheated under the same conditions to yield additional low boiling C_8F_{12}. However, no infusible solid was formed in this reaction.

The isomerization of hexafluorobutadiene dimer was also carried out in the vapor phase. The 30-cm. middle section of a 60 × 3 cm. glass tube was heated by an electric combustion tube furnace and the midpoint temperature maintained at 500 ± 10° while 187.7 g. of C_8F_{12}, b. p. 96 to 100°, was passed through the tube at a rate of 11.7 ± 1.8 g. per hour. No carbonization and only slight etching of the tube was observed. The reaction product, 184 g., was collected at room temperature. Only 0.2 g. was recovered from a Dry Ice trap and nothing condensed in a liquid oxygen trap arranged in series. Distillation yielded the following fractions: 12.1 g. Dry Ice trap-condensate; 114.3 g., b. p. 78 to 83°; 7.7 g., b. p. 83 to 95°; 44.0 g., b. p. 95 to 101°; 3.1 g. residue. The fraction of b. p. 78 to 83° was chlorinated but very little chlorine absorption was observed. The chlorination product was fractionally distilled and neglecting a small forerun and residue boiled sharply at 80°. This fraction had a freezing point of 40.1° (cooling curve) and was saturated to permanganate in acetone.

Anal. Calcd. for C_8F_{12}: C, 29.65; mol. wt., 324.1. Found (80° b. p. fraction): C, 29.8, 29.9; mol. wt., 321, 323.

The Dry Ice trap condensate was shown to consist of hexafluorocyclobutene and low boiling C_8F_{12}.

The fraction of b. p. 95 to 101° was recycled through the hot tube at 500° and the product fractionally distilled to yield: 0.2 g. of Dry Ice trap condensate; 3.7 g., b. p. 89 to 95°; 36.4 g., b. p. 95 to 100°; 2.0 g. residue. No low boiling C_8F_{12} was recovered. The fraction of b. p. 95 to 100° was chlorinated and distilled at 20 mm. pressure to yield: 1.2 g. Dry Ice trap condensate; 37.0 g., b. p. 96 to 100°; 0.7 g. residue. The composition of the fraction b. p. 96 to 100° at 20 mm., $n^{20}D$ 1.3952, was shown to be $C_8Cl_4F_{12}$.

Anal. Calcd. for $C_8Cl_4F_{12}$: C, 20.62; Cl, 30.44. Found: C, 20.5; Cl, 30.7.

Hexafluorobutadiene Trimer.—The trimer of hexafluorobutadiene underwent polymerization on heating. A 50.0-g. sample of $C_{12}F_{18}$, b. p. 65 to 66° at 10 mm. was heated at 300° for one hundred and sixteen hours in a sealed glass tube. Distillation of 48.6 g. of the product through a short Vigreux column at 10 mm. yielded the following fractions: 4.2 g., Dry Ice trap condensate; 16.8 g., b. p. 62 to 68°; 26.3 g., residue. The unsaturation of the recovered $C_{12}F_{18}$ fraction, b. p. 62 to 68° at 10 mm., and the starting material were compared by measuring the volume of potassium permanganate solution required to produce a lasting pink color under identical conditions. No difference in unsaturation was detected. Distillation of 24.0 g. of the residue from a Claisen flask yielded 7.1 g., b. p. 175 to 200° at 10 mm., and a residue which did not distill with a final bath temperature of 320° and 1.5 mm. pressure. By comparison with the boiling points reported for fluorocarbons,[30] the distillate was indicated as probably a C_{24} fraction. When the trimer was passed through a nickel tube at 520° with a contact time of ten seconds, depolymerization occurred. Approximately 15% was converted into hexafluorocyclobutene and 20% into the low boiling C_8F_{12} isomer.

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[28] The chlorination experiments were carried out by R. L. Ehrenfeld.

[29] This experiment was carried out by Oscar Blum.

[30] Grosse and Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

Acknowledgment.—We are greatly indebted to Mr. Oscar Blum, Mr. R. L. Ehrenfeld, and Dr. F. H. Winslow for permission to quote from their experimental work and to Miss Pearl Foster, Dr. Frank McKenna, Mr. J. M. Phelan, and Mrs. Rebecca Teston for analytical determinations.

Summary

Hexafluorobutadiene has been shown to be a highly reactive compound resembling in general butadiene rather than the relatively inert hexachlorobutadiene.

The thermal reactions of hexafluorobutadiene were investigated over the temperature range 150 to 180° and hexafluorocyclobutene, dimers, which were formed in largest amount, and trimers isolated as the principal products.

Hexafluorobutadiene dimer and trimer fractions were shown to be mixtures of isomers. On heating, the dimer was partially converted into a remarkable lower-boiling saturated and highly stable isomer for which a fused tricyclic structure was proposed. Hexafluorobutadiene trimer polymerized slowly on heating. Both dimer and trimer were partially depolymerized by passing through a hot tube.

ITHACA, N. Y. RECEIVED AUGUST 21, 1948

[CONTRIBUTION FROM THE LABORATORY OF EXPERIMENTAL THERAPEUTICS, U. S. PUBLIC HEALTH SERVICE, AND JOHNS HOPKINS SCHOOL OF HYGIENE AND PUBLIC HEALTH]

Disproportionation of Aromatic Stiboso Compounds. I. Mechanism[1]

BY H. H. JAFFE[2] AND G. O. DOAK[2]

Stibosobenzene and its derivatives are known to disproportionate in the solid state at moderately elevated temperatures according to the equation[3]

$$4ArSbO \longrightarrow (Ar_2Sb)_2O + Sb_2O_3$$

In order to determine the mechanism of this reaction and possibly to elucidate the effect of structure on the stability of the carbon–antimony bond we have chosen to investigate the rate of the above reaction. The present paper is concerned with stibosobenzene alone: the effect of substitution will be presented in a later paper.

Experimental

Benzenestibonic acid, prepared by a method described previously,[4] was reduced in concentrated hydrochloric acid and ethyl alcohol with sulfur dioxide in the presence of a trace of hydriodic acid. The resulting solution of phenyldichlorostibine was hydrolyzed by dilute aqueous ammonia or sodium hydroxide.[3] The precipitated stibosobenzene was washed with 10 to 12 liters of water, alcohol and ether, and dried *in vacuo*.

Stibosobenzene, prepared in this manner, was obtained as an amorphous colorless solid, soluble in formic and acetic acids, but insoluble in other common organic solvents and in water. So far it has not been possible to prepare it in a crystalline state. The compound does not possess a well-defined melting point, but sinters at approximately 154°, although this temperature varies somewhat with the rate of heating. The molecular weight is unknown. Cryoscopic measurements in formic and acetic acids gave anomalously large depressions, probably due to reaction with the solvents. By analogy with antimony trioxide which exists in a bimolecular and a polymolecular form,[5] and with aromatic arsenoso compounds, which have molecular weights four times the formula weight,[6] stibosobenzene is probably not monomolecular.

In preliminary experiments it was demonstrated that the disproportionation of stibosobenzene at 100° yielded bis-(diphenylantimony)-oxide in quantitative yield. The product was identified by melting point and analysis. In an atmosphere of nitrogen no side reaction could be detected. It was further shown that extraction of a mixture of stibosobenzene, antimony trioxide and bis-(diphenylantimony)-oxide with five portions of ether (40 ml. each) permitted quantitative recovery of the bis-(diphenylantimony)-oxide, without contamination with stibosobenzene or antimony trioxide.

To determine the rate of disproportionation, samples of stibosobenzene (0.25 to 0.75 g.) were permitted to rearrange in large test-tubes in an atmosphere of nitrogen in a constant temperature bath maintained at fixed temperatures between 75 and 100°. Samples were withdrawn at accurately measured intervals, chilled in ice and extracted with ether. The extracts were evaporated *in vacuo* at room temperature and dried to constant weight. The bis-(diphenylantimony)-oxide was weighed and analyzed and the fraction of the original material that had rearranged was obtained from these data. The rate constants, k_2, were calculated from equation (1) below by the method of least squares using from 6 to 14 experimental points.

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(2) Present address: Syphilis Experimental Laboratory, School of Public Health, University of North Carolina, Chapel Hill, North Carolina.

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