

Fluoro-olefin Chemistry. Part 12.¹ Some Reactions of 3,4-Dihalogeno-tetrafluorocyclobutenes: a Synthesis of Perfluorocyclo-octatetraene

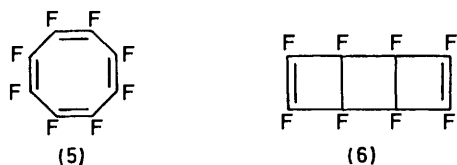
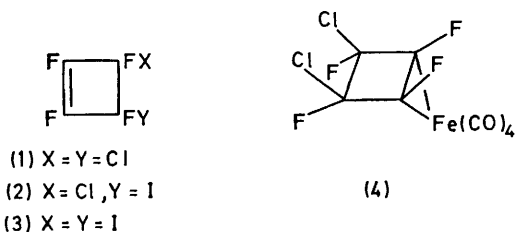
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Unsuccessful attempts have been made to dehalogenate 3,4-dichlorotetrafluorocyclobutene and 3-chlorotetrafluoro-4-iodocyclobutene. The dichlorocyclobutene yields an unstable complex $(\pi\text{-C}_4\text{F}_4\text{Cl}_2)\text{Fe}(\text{CO})_4$ with $\text{Fe}_2(\text{CO})_9$. Tetrafluoro-3,4-di-iodocyclobutene gives perfluorocyclo-octatetraene (58%) upon pyrolysis at 250 °C, and in addition to the cyclo-octatetraene (31%), perfluorostyrene (24%), and tetrafluoro-1,4-di-iodobuta-1,3-diene (37%) upon pyrolysis at 580 °C and 0.1 mmHg. With zinc dust, isomeric cyclobutenes are formed by fluorine migration, and the coupled product from copper bronze also results from fluorine migration. With phenylacetylene at 200 °C, 1,2,3,4-tetrafluorobiphenyl (12%) is obtained.

CYCLOBUTADIENE and its derivatives have aroused much theoretical and experimental interest,² but there have been very few reports of fluorinated derivatives.³ The recent report of tetrafluorocyclobutadiene,⁴ obtained by photolysis of tetrafluorocyclobutene-3,4-dicarboxylic anhydride and trapped as its dimer and as a Diels-Alder adduct with furan, prompts us to describe our investigations in this area, which have yielded a number of novel results, and in particular provided a route to perfluoro-cyclo-octatetraene.

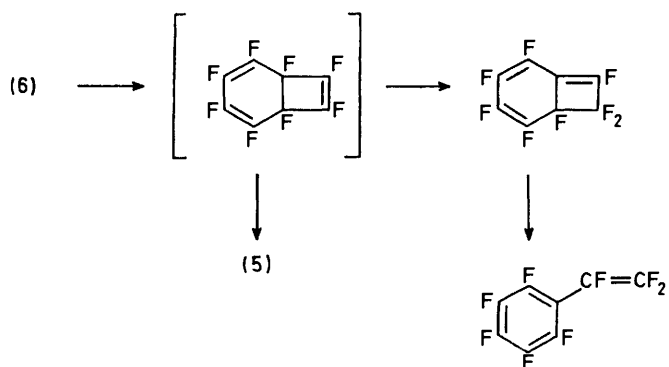
3,4-Dichlorotetrafluorocyclobutene (1) is an attractive starting material, since it may readily be obtained in four easy steps from the commercially available 1,1,2,2-tetrachlorodifluoroethane.⁵ Furthermore, stepwise replacement of chlorine by iodine to give compounds (2) and (3) occurs readily with sodium iodide in acetone.⁶

Unsuccessful attempts were made to dechlorinate compound (1) with sodium and magnesium amalgams, zinc, pentacarbonyliron, and disodium tetracarbonyliron(-II). The reaction of enneacarbonyldi-iron with *cis*-3,4-dichlorocyclobutene provides a complex $(\pi\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ which is a convenient precursor for cyclobutadiene.⁷ In contrast, compound (1) (*cis*:*trans* ratio 45:55) yielded the unstable *cis*-complex (4), in which the fluorines of the CFCl groups are *cis* to the iron from their



low field shift in the n.m.r. spectrum. The complex gave unchanged olefin upon decomposition and there was no transfer of chlorine to iron. Similar complexes have been obtained with a large number of fluoro-olefins.⁸

Reactions with the chloro-iodo-compound (2) were similarly unsuccessful. Reaction with lithium metal resulted in tar formation, lithium amalgam gave a low yield of dichlorocyclobutene (1), presumably by exchange involving metal chloride, no reaction occurred



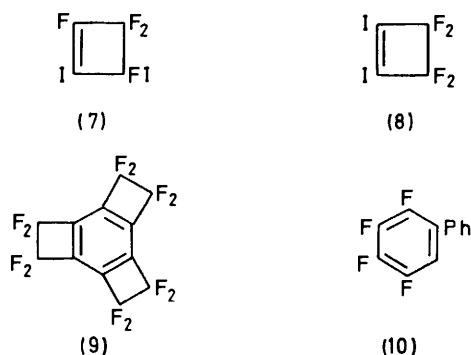
SCHEME 1

with copper bronze at 160 °C, copper powder in bis-(2-methoxyethyl) ether resulted in some replacement of iodine by hydrogen, and exchange occurred with *n*-butyl-lithium, as evinced by the formation of butyl iodide, but no volatile fluorine-containing compounds were obtained.

Reactions of 3,4-di-iodotetrafluorocyclobutene (3) were somewhat more successful, if in an unexpected manner. Its photolysis in the presence of mercury to give polymeric material,⁶ and small amounts of a cyclic trimer of tetrafluorocyclobutadiene,⁹ have been previously described. No reaction occurred with enneacarbonyldi-iron, and nickel carbonyl yielded an unidentified cream-yellow powder which contained little fluorine. Static pyrolysis of the cyclobutene (3) at 250 °C yielded perfluorocyclo-octatetraene (5) (58%). This has recently been obtained by thermal rearrangement of tetrafluorocyclobutadiene dimer (6) at 150 °C, or directly from tetrafluorocyclobutadiene if 'hot' (6) is not collision deactivated as it is formed.⁴ There is no evidence that tetrafluorocyclobutadiene is involved here, but it provides a convenient route to perfluorocyclo-octatetraene, readily scaled up and less hazardous than the alternative route, which involves ozonolysis of hexafluorobicyclo[2.2.0]hexa-2,5-diene. Flow pyrolysis

of the cyclobutene (3) at 575–580 °C and 0.1 mmHg yielded perfluorocyclo-octatetraene (31%) and, unexpectedly, perfluorostyrene (24%), together with recovered di-iodocyclobutene and the *E,E*-, *E,Z*-, and *Z,Z*-isomers of tetrafluoro-1,4-di-iodobuta-1,3-diene (37%). Perfluorostyrene does not arise by thermal rearrangement of perfluorocyclo-octatetraene, and it is tempting to suggest the mechanism of Scheme 1, involving a [1,3] fluorine shift.

Pyrolysis of the iodocyclobutene in the presence of zinc dust or copper bronze to remove iodine and perhaps to aid tetrafluorocyclobutadiene formation was investigated. With zinc, only 15% perfluorocyclo-octatetraene was obtained at 160 °C, most of the butene isomerizing to the cyclobutenes (7) and (8). An analogous rearrangement of the dichlorocyclobutene (1) takes place in the presence of nickel fluoride.¹⁰ With copper bronze at



160 °C, cyclo-octatetraene (16.5%) and compound (9) (11%), previously obtained from the iodocyclobutene (8),¹¹ were formed. Pyrolysis of the iodocyclobutene (3) in the presence of phenylacetylene gave 2,3,4,5-tetrafluorobiphenyl (10) (12%), a reaction which offers promise for the preparation of 1,2-disubstituted tetrafluorobenzenes.

EXPERIMENTAL

Volatile materials were handled in a conventional vacuum system. ¹⁹F N.m.r. spectra were determined at 94.1 MHz on a Varian HA 100 spectrometer. Values of δ_F are in p.p.m. to high field (positive) of trifluoroacetic acid. Mass spectra were determined at 70 eV on an A.E.I. MS902 instrument.

3,4-Dichlorotetrafluorocyclobutene was obtained by the thermal cyclization of 1,4-dichlorotetrafluorobuta-1,3-diene,⁵ and 3-chloro-tetrafluoro-4-iodo- and tetrafluoro-3,4-di-iodo-cyclobutenes by the reaction of the dichlorocyclobutene with sodium iodide in refluxing acetone.⁶

Reactions of 3,4-Dichlorotetrafluorocyclobutene.—(a) *Attempted dechlorinations.* The dichlorocyclobutene was recovered unchanged when heated with activated zinc dust at temperatures up to 135 °C for 18 h, with or without bis-(2-methoxyethyl) ether as solvent. At 200 °C for 18 h without solvent, 50% conversion to 1,4-dichlorotetrafluorobuta-1,3-diene resulted.

The cyclobutene was recovered from attempted reaction with magnesium amalgam in bis-(2-methoxyethyl) ether at 120 °C for 2 days, and with sodium amalgam in pentane or bis-(2-methoxyethyl) ether at room temperature for 2 days;

with the latter solvent no reaction occurred in the presence of naphthalene or benzophenone as electron carriers.

(b) *With iron carbonyls.* No products were obtained from thermal (75–80 °C for 4 h) or photochemical (u.v. in silica) reaction with pentacarbonyliron.

Enneacarbonyldi-iron (2.0 g, 5.5 mmol) and an excess of 3,4-dichlorotetrafluorocyclobutene (6 g, 30.8 mmol) (*cis*:*trans* 45:55), were sealed in a silica tube (300 ml) and irradiated with shaking with u.v. light (Hanovia SP500 lamp at a distance of 25 cm) for 72 h. Volatile material was removed *in vacuo* and shown (i.r.) to comprise the cyclobutene and pentacarbonyliron, and the residue was extracted with pentane and chromatographed on Florisil (pentane eluant) and sublimed at 30–40 °C and 1 mmHg to give lemon yellow crystals of *cis*-3,4-dichlorotetracyclobutene(tetracarbonyl)iron, which was identified by mass spectrometry, *m/e* (only ³⁵Cl containing ions are reported) 327 (0.2, *M* – Cl), 194 (60.1, C₄F₄Cl₂), 168 (45.6, C₄O₄Fe), 159 (100, C₄F₄Cl), 140 (52.5, C₃O₃Fe), 109 (95.7, C₃F₂Cl), 93 (56.7, C₃F₃), and 84 (62.2%, COFe), and i.r. spectroscopy, ν_{\max} . 2 110s, 2 040s, 2 010s (C=O str), 1 380w, 1 225m, 1 175m, 1 045m, 975m, 835s, and 758w cm⁻¹. The ¹⁹F n.m.r. spectrum (10% w/v in pentane) showed bands due to *cis*-3,4-dichlorocyclobutene, and at δ_F 8.6 (CFCl) and 79.0 p.p.m. (CF₂Fe), and the complex readily decomposed on standing, giving the original cyclobutene.

No iron complex was obtained from reaction of the cyclobutene with an excess of disodium tetracarbonyliron in tetrahydrofuran at room temperature and at 60–65 °C for 2 h.

Attempted Dehalogenation of 3-Chlorotetrafluoro-4-iodocyclobutene.—A solution of the cyclobutene (6.8 g, 23.6 mmol) in tetrahydrofuran (35 ml) was added dropwise to lithium amalgam (50 g, 0.66% w/w) and tetrahydrofuran (10 ml) at 50–60 °C over 2 h, to give a dark and gelatinous product. Volatile material was removed *in vacuo* at room temperature, water (50 ml) added, the lower fluorocarbon layer (2.9 g) was dried, and separated by g.l.c. (2 m SE-30 at 90 °C) to give recovered chloriodocyclobutene (1.9 g, 6.5 mmol, 28%) and 3,4-dichlorotetrafluorocyclobutene (0.24 g, 1.2 mmol, 5%). The residue yielded only mercury(II) iodide upon extraction with chloroform.

When the cyclobutene was added to lithium shavings in tetrahydrofuran at 0 °C, the metal rapidly became coated by a brown-black layer, and only recovered cyclobutene (73%) was obtained.

The cyclobutene was heated with freshly precipitated copper powder in bis-(2-methoxyethyl) ether at 120–130 °C for 6 h, but g.l.c.–mass spectrometry indicated that the volatile product (1.2 g) was comprisingly mainly of reduction products (two isomers of C₄F₄HCl and one of C₄F₄H₃Cl).

The cyclobutene failed to react when passed over copper powder at 180–190 °C, although some ring-opening to 1-chlorotetrafluoro-4-iodobuta-1,3-diene occurred,¹² and it was partially destroyed (CO₂ and SiF₄ formation) at 300–320 °C. The cyclobutene was recovered (95%) when heated with copper bronze at 165–170 °C for 6 h.

To a solution of the cyclobutene (2.12 g, 7.6 mmol) in diethyl ether (5 ml) at –100 °C was added dropwise a solution of *n*-butyl-lithium (6 ml of a 1.52M solution in diethyl ether, 9.1 mmol) over 30 min, when vigorous reaction occurred. The mixture was maintained at –78 °C for 30 minutes, then slowly warmed to room temperature. The volatile material was shown by g.l.c. and g.l.c.–mass spectrometry to comprise diethyl ether, *n*-butyl bromide

n-butyl iodide, and recovered cyclobutene. The tarry residue contained Cl^- and I^- .

Reactions of Tetrafluoro-3,4-di-iodocyclobutene.—(a) *With metal carbonyls.* The cyclobutene and pentacarbonyl-iron, heated *in vacuo* at 65–70 °C for 10 h yielded after extraction with light petroleum (60–80 °C) a tarry red gum, shown by t.l.c. to consist of several components, but no identifiable products were obtained by chromatography.

No reaction was detected with enneacarbonyl-iron in diethyl ether at room temperature for 4 h, then 30–35 °C for 2 h.

An excess of nickel carbonyl and the cyclobutene in diethyl ether at room temperature for 3 days gave a thick yellow precipitate, Soxhlet-extracted with chloroform to give an unidentified sparingly soluble powder (Found: C, 14.1; H, 3.5; F, 4.3%).

(b) *Thermolysis.* The cyclobutene (17.4 g, 46 mmol), sealed *in vacuo* in a 250 ml Pyrex tube and heated at 250 °C for 8 h, gave iodine, removed by shaking with zinc dust, and volatile material (4.0 g), shown by g.l.c. (2 m TXP at 70 °C) to contain starting material (10%) and a component, separated by g.l.c. (at 100 °C) and identified as perfluorocyclo-octatetraene (3.3 g, 13.3 mmol, 58%) (Found: C, 38.5; F, 61.1. Calc. for C_8F_8 : C, 38.7; F, 61.3%), m.p. 40–41 °C (lit.⁴ 41–41.5°), δ_{F} 45.0, ν_{max} 1 724 and 1 695 cm^{-1} (CF=CF str) (lit.⁴ 1 724 and 1 692 cm^{-1}), *m/e* 248 (C_8F_8 , 91), 229 (C_8F_7 , 42), 198 (C_7F_6 , 59), 186 (C_6F_5 , 20), and 179 (C_7F_5 , 100%). Ether extraction of the residue afforded a fluorinated (i.r.) gum.

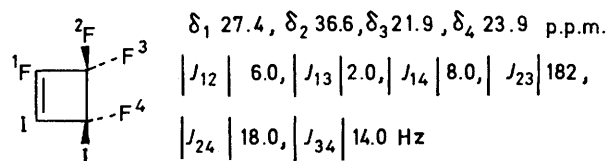
The cyclobutene (6.4 g, 16.9 mmol), passed through a silica tube (500 mm heated length, 22 mm i.d.) at 575–580 °C and 0.1 mmHg (contact time *ca.* 0.5 s), gave, after removal of iodine with mercury, a product (4.1 g) shown by g.l.c. (2 m SE-30 at 90 °C) to contain seven components in the molar ratio 21:16:8:4:6:29:16. The first two components were separated by fractionation *in vacuo* and separated by g.l.c. (2.5 m SE-30 at 55 °C) to give perfluorocyclo-octatetraene and perfluorostyrene, identified by ^{19}F n.m.r.¹³ and i.r. spectroscopy and mass spectrometry. The higher-boiling fraction was separated by g.l.c. (2 m SE-30 at 140 °C) to give *trans*- and *cis*-tetrafluoro-3,4-di-iodocyclobutene, identified by i.r. and n.m.r. spectroscopy, and, in order of elution, the *E,E*-, *E,Z*-, and *Z,Z*-isomers of tetrafluoro-1,4-di-iodobuta-1,3-diene, identified by ^{19}F n.m.r.¹² and i.r. spectroscopy, with, respectively, C=C stretching bands at ν_{max} 1 690w and 1 655w, 1 655m and 1 620m, and 1 652 and 1 622 cm^{-1} . They had almost identical mass spectra; the *E,E*-isomer had *m/e* 378 ($\text{C}_4\text{F}_4\text{I}_2$, 39), 251 ($\text{C}_4\text{F}_4\text{I}$, 100), 124 (C_4F_4 , 49), and 93 (C_3F_3 , 17%).

(c) *With air.* A similar flow pyrolysis in the presence of 0.2–0.3 mmHg of air gave in addition to the above compounds, difluoromaleic acid, identified by i.r. spectroscopy and mass spectrometry with *m/e* 152 (*M*, 7), 135 ($\text{C}_4\text{HF}_2\text{O}_3$, 6), 108 ($\text{C}_3\text{H}_2\text{F}_2\text{O}_2$, 18), 91 ($\text{C}_3\text{HF}_2\text{O}$, 7), 88 (C_3HFO_2 , 16), 63 (C_2HF_2 , 15), 45 ($\text{C}_2\text{H}_2\text{F}$, 38), and 44 (CO_2 or C_2HF , 100%).

(d) *With zinc dust.* The di-iodocyclobutene (6.4 g, 16.9 mmol) and zinc dust (*ca.* 20 g), sealed in a 250 ml Pyrex tube and heated at 160 °C for 24 h, gave volatile material (5.6 g) shown by g.l.c. (2 m SE-30 at 110 °C) to contain perfluorocyclo-octatetraene (15%) and recovered cyclobutene together with two other components of very similar retention time, which were shown to be tetrafluoro-2,3-di-iodocyclobutene with ν_{max} 1 681 cm^{-1} (CF=CI str), *M* 378 (by mass spectrometry), and the ^{19}F n.m.r. para-

meters in Scheme 2 and tetrafluoro-1,2-di-iodocyclobutene, with δ_{F} 33.2 p.p.m. (lit.,¹¹ 35 p.p.m.), ν_{max} 1 553w cm^{-1} (lit.,¹¹ 1 550 cm^{-1}), and *M* 378 (by mass spectrometry).

(e) *With copper bronze.* Activated copper bronze (5 g) and the cyclobutene (11.1 g, 29.4 mmol), sealed in a 250 ml Pyrex tube and heated at 160 °C for 6 h, gave volatile material (0.6 g) shown by i.r. spectroscopy and g.l.c. to be very largely perfluorocyclo-octatetraene (16.5%), and an off-white crystalline solid which was sublimed out at 50–60 °C and 0.1 mmHg, crystallized from light petroleum (60–80 °C) and sublimed to give perfluoro(hexahydrotricyclobutenobenzene) (0.41 g, 1.1 mmol, 11%) (Found: C, 39.0; F, 60.9%. Calc. for $\text{C}_{12}\text{F}_{12}$: C, 38.7, F, 61.3%), m.p. 125–130 °C (sublimes) (lit.,¹⁰ 133–134 °C), δ_{F} 27.2 p.p.m. (lit.,¹⁰ 26.9 p.p.m.), ν_{max} 1 633 and 1 400 cm^{-1} (lit.,¹¹ 1 633 and 1 401 cm^{-1}), and *M* 372 (by mass spectrometry). Extraction of the residue with diethyl ether yielded a brown viscous oil, which was not further investigated.



SCHEME 2

(f) *With phenylacetylene.* Phenylacetylene (6.6 g, 64.6 mmol) and the cyclobutene (12.2 g, 32.3 mmol), sealed in a 250-ml Pyrex tube and heated at 200 °C for 3 h, gave volatile material which was very largely hydrogen iodide, and a black carbonaceous mass, which was extracted with diethyl ether; iodine was removed (Na_2SO_3) from the extract, which was dried (MgSO_4) and the solvent removed to yield a solid, recrystallized from light petroleum (30–40 °C) to give 2,3,4,5-tetrafluorobiphenyl (0.89 g, 3.9 mmol, 12%), m.p. 73–74 °C (lit.,¹⁴ 75–76 °C), identified by n.m.r. and i.r. spectroscopy, and mass spectrometry.

Thermal and Photochemical Stability of Perfluorocyclo-octatetraene.—The cyclo-octatetraene, when passed at 0.1–0.2 mmHg four times through a silica tube heated to 580–600 °C, was unchanged (i.r.). When a sample was sealed in a silica n.m.r. tube and irradiated with u.v. light (Hanovia UVS 500 lamp) for 3 days, it showed no change by n.m.r. spectroscopy.

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