15 min a solution of 57 mg of crude aldehyde **2a** in 5.5 ml of dry tetrahydrofuran was added quickly. Upon further stirring at room temperature for 30 min the mixture was refluxed for 4 hr, then diluted with 75 ml of ether and filtered through Celite. The filtrate was evaporated under vacuum and the residue rinsed thoroughly with water and extracted with ether. The extract was dried over magnesium sulfate and evaporated. The solid residue was purified by two successive preparative TLC operations on silica gel (one by elution with chloroform and the second with ether). Crystallization of the colorless solid, 45 mg, from ether yielded colorless needles of diene **2b:** mp 192–193.5°; $[\alpha]^{24}D$ +10.3° (*c* 1.6, EtOH); ir ($CHCl_3$) OH 3670 (w), 3615 (m), 3450 (m), C=C 1631 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 0.84, 0.88, 1.04 (s, 3 each, methyls), 3.12, 3.39 (AB pair of d, 1 each, J = 11.0 Hz, OCH_2), 4.65, 4.69, 4.71, 4.74, 4.87, 4.90, 4.95, 4.98, 5.49, 5.64, 5.78, 5.93 (ABX lines, 3, vinyl H's), 5.18 (broad s, 1, nuclear olefinic H); MS *m/e* (rel intensity) 304 (M^+, 9), 286 (40), 256 (33), 187 (100). Anal. *m/e* 304.2399 (calcd for $C_{20}H_{32}O_2$, 304.2401).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.75; H, 10.46.

Registry No.—**1**, 56816-57-0; **2a**, 56783-50-7; **2b**, 56783-51-8.

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Preparation of Mono- and Diiodocyclopropene

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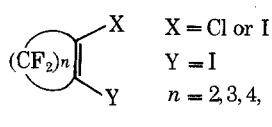
A variety of methods used for the preparation of mono- and diiodoperfluorocycloalkenes possessing the general structure shown below have been previously reported.[1–3]



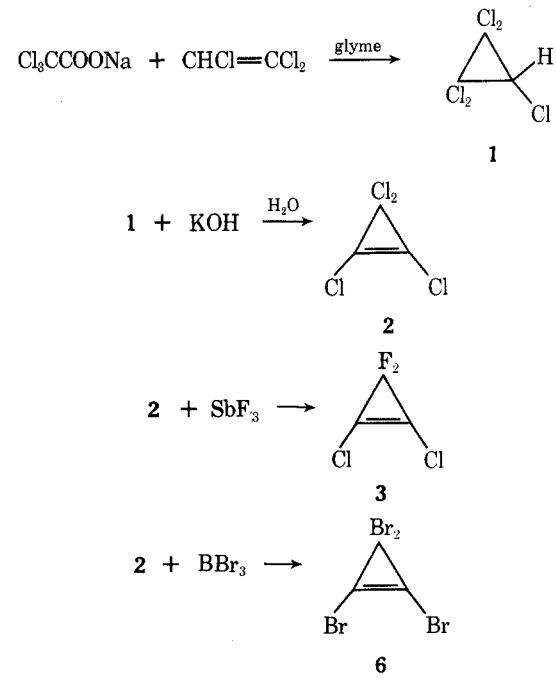
X = Cl or I
Y = I
n = 2, 3, 4,

These perfluorovinyl iodides have shown unique synthetic utility in copper coupling reactions[4,5] and in the preparation of various organometallic derivatives.[6,7]

Previous attempts to prepare the iodo derivatives of the highly strained cyclopropene system (where n = 1) have been unsuccessful.[8] Although many perhalocyclopropenes have been prepared, including tetrabromocyclopropene,[9] a recent report indicated that iodocyclopropenes are expected to be very unstable.[10]

We wish now to report on a facile synthesis of 1-chloro-2-iodo-3,3-difluorocyclopropene (**5**) and 1,2-diiodo-3,3-difluorocyclopropene (**4**). These compounds are readily distilled under vacuum and darken slowly on standing and exposure to sunlight. Studies on the reactions of **4** and **5** with copper powder and various nucleophiles are being investigated and will be reported in another paper.

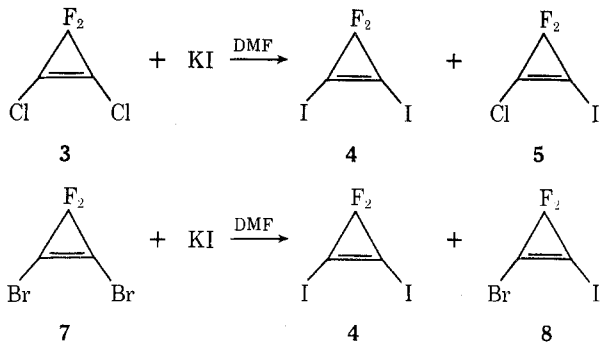
The method of Tobey and West[9] was used to prepare 1,2-dichloro-3,3-difluorocyclopropene (**3**). We have introduced several changes in this procedure which have increased the overall yield of **3** eightfold. The principal changes occur in the first and third step below.



The yield of pentachlorocyclopropane (**1**) was doubled by employing approximately half the quantity of glyme previously suggested. This change causes the decomposition of sodium trichloroacetate to proceed more slowly; however, there are fewer by-products arising from the reaction of glyme with the generated dichlorocarbene.

A significant improvement in the reaction of tetrachlorocyclopropene (**2**) with SbF_3 has been obtained by using freshly sublimed SbF_3. The reaction initiates at a much lower temperature and the distillate contains nearly pure **3** in 76% yield. Sublimed SbF_3 permits only trace amounts of the monofluoro product (3-fluoro-1,2,3-trichlorocyclopropene) to be formed even when **2** is used in excess. This would tend to give further support to a proposed intermediate involving both allylic chlorine atoms of **2** and three fluorine atoms in a tight coordination sphere around a pentacoordinated antimony.[9]

Previous studies on the reaction of anhydrous KI with 1,2-dichloroperfluorocycloalkenes in DMF indicated that the degree of substitution, yields, and reaction rates were largely determined by ring size or strain energies of the perfluorocycloalkene.[1] It was not surprising to observe that **3** reacted with KI in DMF at room temperature.



The monoiodide **5** was obtained in a 57% yield by allowing **3** and KI (1:1.2 molar ratio) in DMF to react overnight at room temperature. By contrast, the corresponding cyclopentene and cyclohexene with KI (1:2 molar ratio) gave only 45 and 9% of the monoiodides after 19 and 134 hr reflux, respectively. Cyclobutene gave 36% mono- and 26% diiodides after 5 hr reflux under similar conditions.[1]

When the molar ratio of **3** to KI was changed to 1:5 only the diiodide **4** was isolated in a 60% yield. A similar reaction using 1,2-dibromo-3,3-difluorocyclopropene (**7**) and KI in a 1:5 ratio gave the diiodide **4** in an 87% yield. Using a 1:1.5 ratio of the dibromide **7** and KI gave a 60% yield of 1-bromo-2-iodo-3,3-difluorocyclopropene (**8**) and a small quantity of the diiodide **4**. These compounds could not be separated by simple distillation and required preparative VPC to isolate a pure sample of **8**.

The ir spectra of the 1,2-dihalo-3,3-difluorocyclopropenes are quite similar, showing only five principal absorptions. The carbon–carbon double bond stretch appeared as a weak band from 1729 cm^{-1} for **5** down to 1656 cm^{-1} for **4**. This band is absent in 1,2-dichloro-3,3-difluorocyclopropene; however, it is found at the highest recorded value in perfluorocyclopropene (1945 cm^{-1}).[11]

The other principal bands of 1,2-dihalo-3,3-difluorocyclopropenes appeared at 1310 ± 30, 1090 ± 25, 835 ± 15, and 725 ± 30 cm^{-1}. These bands form a smooth linear relationship when the position of their absorption is plotted against the sum of the square root of the molecular weight of the halogen atoms in the 1 and 2 position of cyclopropene.

The mass spectra of **4, 5,** and **8** are similar to the spectra reported previously for bromo- and chlorotrifluorocyclopropene.[10] The base peaks appear as the trihalopropenium ion produced through the preferential loss of bromine or iodine from a vinylic position and not through loss of fluorine from the allylic position.

The ^{19}F NMR spectra for **4, 5,** and **8** showed only a sharp singlet arising from the geminal fluorine atoms in the allyic position. Their values are shifted slightly from those reported earlier for 1,2-dichloro-3,3-difluorocyclopropene.[10]

Experimental Section

Commerically available trichloroethylene, dimethylformamide, and glyme (1,2-dimethoxyethane) were dried and purified according to known procedures.[12] Antimony trifluoride (PCR, Inc.) was freshly sublimed (220°, 0.03 mm) prior to each reaction. All temperatures are uncorrected. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo. Fluorine NMR were obtained on a Varian 56/60 using F-11 as an internal standard. The mass spectra were obtained on a Du Pont 21-491 instrument and the ir spectra were obtained on a Beckman IR-8 and calibrated at 1601.0 cm^{-1}.

Pentachlorocyclopropane (1). A slurry of sodium trichloroacetate (350 g, 1.89 mol) in 1300 ml of trichloroethylene was mechanically stirred and heated to gentle reflux for 3 hr. During this time approximately 0.1 ml of H_2O was collected in a Dean-Stark trap. The water trap was removed and 200 ml of glyme was added. The mixture was heated to gentle reflux (92–94°) for 5 days. Evolution of CO_2 was slow and uniform during this period. The reaction mixture was washed repeatedly with water, dilute HCl, and finally water and then dried over $CaCl_2$. The excess trichloroethylene was removed by fractional distillation and the higher boiling residue distilled under vacuum. The fractions boiling between 80 and 85° (31 mm) gave 189 g (47%) of **1**, $n^{34.0}D$ 1.5110 [lit.[9] bp 57° (7 mm), $n^{27.5}D$ 1.5170].

Tetrachlorocyclopropene (2). To a solution of 35.5 g of 95% KOH in 40 ml of water was added 50.0 g (0.233 mol) of **1**. The two-phase mixture was stirred slowly and heated to 75° where a spontaneous reaction initiated. The heat was removed and the temperature rose to 88° where it was maintained by occasional ice cooling. After 25 min the mixture was cooled to 50° and 50 ml of ice water and then 25 ml of cold concentrated HCl were added. The organic layer was taken up in CH_2Cl_2, washed with water, and dried ($CaCl_2$). Fractionation of the CH_2Cl_2 extracts gave 32.0 g (77%) of **2**, bp 71–72° (98 mm). $n^{21.0}D$ 1.5054 [lit.[9] bp 130–131° (745 mm), $n^{25.0}D$ 1.5065].

1,2-Dichloro-3,3-difluorocyclopropene (3). Antimony trifluoride (20.0 g, 0.112 mol) and 15.0 g (0.084 mol) of **2** were placed into a 25-ml flask fitted with a 150-mm Vigreux column and distillation head. The reaction mixture was heated to 110–115° over a 40-min period during which time 9.3 g (76%) of a colorless liquid (bp 58–61°) collected in an ice-cooled receiver. Chilled water was circulated through the distillation head condenser. Analysis by VPC of the distilled product indicated that it was essentially pure **3**, $n^{26.0}D$ 1.4045 [lit.[9] bp 60° (733 mm), $n^{25.0}D$ 1.4032].

1,2-Diiodo-3,3-difluorocyclopropene (4). A solution of 28.6 g (0.172 mol) of KI in 78 ml of DMF was cooled to 19° and 5.0 g (0.034 mol) of **3** was added dropwise. After stirring at room temperature for 1.5 hr the mixture was heated to 70° for 5 hr and then left overnight at room temperature. The darkened mixture was diluted with water and then steam distilled and the distillate extracted with CH_2Cl_2. The combined extracts were dried ($CaCl_2$) and fractionated, yielding 6.8 g (60%) of **4**: bp 82–85° (35 mm); $n^{25}D$ 1.5920; ir (neat film) 1656 w, 1280 s, 1065 s, 819 s, and 694 cm^{-1} s; MS *m/e* 328 (M^+), 309, 278, 201 (base peak), and 74. The ^{19}F NMR spectrum gave a singlet at 100.5 ppm upfield from F-11 (Cl_3CF).

Anal. Calcd for $C_3F_2I_2$: C, 10.98; F, 11.59; I, 77.41. Found: C, 11.19; F, 11.90; I, 76.85.

1-Chloro-2-iodo-3,3-difluorocyclopropene (5). Compound **3** (12.0 g, 0.0828 mol) was added to a solution of 16.49 g (0.0994 mol) of KI in 50 ml of DMF at 18° and then allowed to warm to room temperature overnight. The mixture was steam distilled and the distillate extracted with CH_2Cl_2. The $CaCl_2$-dried extracts were fractionally distilled, yielding 11.1 g (57%) of **5**: bp 64–65° (133 mm); $n^{24.0}D$ 1.4993; ir (neat film) 1729 m, 1300 s, 1080 s, 1080 s, 830 s, and 730 cm^{-1} s; MS *m/e* 238, 236 (M^+) 219, 217, 188, 186, 111, 109 (base peak), and 74. The ^{19}F NMR spectrum gave a singlet at 100.6 ppm upfield from F-11 (Cl_3CF).

Anal. Calcd for C_3F_2ClI: C, 15.24; F, 16.07; Cl, 14.99; I, 53.68. Found: C, 14.97; F, 16.07; Cl, 15.22; I. 53.27.

The small amount of undistilled liquid was principally **4**.

Tetrabromocyclopropene (6). The procedure of Tobey and West[9] was used to prepare **6**, bp 61–64° (1.1 mm), $n^{26.0}D$ 1.6348 [lit.[9] bp 70–95° (0.1–0.4 mm), $n^{25.1}D$ 1.6344].

1,2-Dibromo-3,3-difluorocyclopropene (7). Freshly sublimed SbF_3 (18.9 g, 0.105 mol) and 23.7 g (0.066 mol) of **6** were placed into a 25-ml flask and attached to a short-path distillation head. The mixture was heated to 118° for 30 min, during which time 12.6 g (81%) of almost pure **7** distilled over at 104°. A second distillation gave **7**, bp 104–105°, $n^{26.0}D$ 1.4752 [lit.[9] bp 105° (742 mm), $n^{25.0}D$ 1.4757].

Reaction of 7 with KI in DMF (1:5 Ratio). Compound **7** (5.00 g, 0.21 mol) was added to a solution of 17.7 g (0.106 mol) of KI in 50 ml of DMF at room temperature, causing the immediate appearance of a fine precipitate. The mixture was stirred at room temperature for 1.5 hr and then heated to 70° for 3 hr. Work-up of the reaction mixture was similar to that described for **4**. Distillation of the CH_2Cl_2 extracts gave 6.1 g (87%) of product, bp 82–83° (35 mm), whose ir spectrum was identical with that of **4**.

Reaction of 7 with KI in DMF (1:1.5 Ratio). Compound **7** (4.00 g, 0.0171 mol) was added to a solution of 4.25 g (0.0256 mol) of KI in 20 ml of DMF at 18° and then allowed to warm to room temperature. Total reaction time was 4.5 hr. Work-up in a manner similar to that described for **4** gave 3.5 g of a crude product (bp 76–100°, 79 mm) which was a mixture of **4** and 1-bromo-2-iodo-3,3-difluorocyclopropene (**8**). A second distillation of the mixture gave 2.9 g (60%) of nearly pure **8** which again contained small

amounts of 4. A VPC-purified sample (25 ft × 0.25 in. column containing 20% SF-1265 on Chromosorb W) gave pure 8: $n^{27.0}$D 1.5326; ir (neat film) 1708 w, 1290 s, 1070 s, 820 m, and 708 cm^{-1} m; MS *m/e* 282, 280 (M^+), 263, 261, 232, 230, 201 (base peak), 155, 153, 127, and 74. The ^{19}F NMR spectrum gave a singlet at 100.5 ppm upfield from F-11 (Cl_3CF).

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Registry No.—1, 6262-51-7; 2, 6262-42-6; 3, 6262-45-9; 4, 56830-73-0; 5, 56830-74-1; 6, 6262-43-7; 7, 6262-46-0; 8, 56840-75-2; sodium trichloroacetate, 2923-18-4; trichloroethylene, 79-01-6; antimony trifluoride, 7783-56-4; potassium iodide, 7681-11-0.

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Reaction of Xenon Difluoride with Polycyclic Aromatic Hydrocarbons. Fluorination of Pyrene

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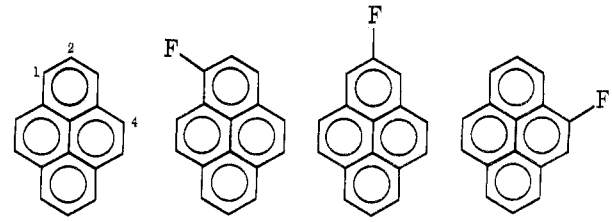
Fluorine-substituted condensed polycyclic aromatic hydrocarbons and heterocyclics are of interest in experimental carcinogenesis.[3–5] Heretofore, their syntheses were based mostly on the following two general methods. (a) A "tailor-made" sequence analogous to the one applied in a well-established synthesis of the corresponding polycyclic hydrocarbon, but with a fluorine-substituted starting material (e.g., 3-fluorophthalic anhydride,[6] 4-fluoro-1-bromonaphthalene[7]). (b) A direct electrophilic substitution of the polycyclic aromatic hydrocarbon followed by appropriate transformations of the substituent to fluorine[8] (e.g., ArH → $ArNO_2$ → $ArNH_2$ → $ArN_2^+BF_4^-$ → ArF and ArH → $ArSO_3H$ → ArOH → ArOCOF → ArF). In the latter method, the fluorine is usually introduced at the most reactive sites of the hydrocarbon. Neither method is very satisfactory. Direct methods for the introduction of a fluorine atom into polycyclic aromatics are still in their infancy. Recently, xenon difluoride has been shown to act as an efficient and selective fluorinating agent for simple aromatic compounds, both in solution and in the vapor phase.[9–14] The reaction is catalyzed by HF and does not proceed without it.[11,15] We report the application of this direct fluorination route in the aromatic polycyclic series. Pyrene (1) was selected as a model substrate for examining the mode of the reaction of xenon difluoride with polycyclic aromatic hydrocarbons. The convenience of pyrene stemmed from its high symmetry (point group D_{2h}), its tetracyclic structure, and the presence of three characteristic substitution sites (1, 2, and 4) which lend themselves readily to identification by ^{19}F NMR spectra (vide infra).



1 2 3 4

The reaction of xenon difluoride and pyrene was carried out in a vacuum line system as well as in an open system. Both experiments were performed under anhydrous conditions. The products were separated from the crude reaction mixture by column chromatography on silica gel.

The major monomeric products of the reaction (apart from the starting material 1), were 1-fluoropyrene (2, 16–22% yield) and 2-fluoropyrene (3, 11–14% yield). Fluorination at the 4 position apparently also occurred, albeit in very low yields. The *patterns* of the ^{19}F NMR absorptions served as a probe for identifying the site of the fluorination. The 1 isomer (2) showed a quartet (at 43.2 ppm, J_1 = 10.0, J_2 = 5.4 Hz) while the 2 isomer (3) showed a triplet (at 38.9 ppm, J = 9.2 Hz). Fluorination at the 4 position was indicated by a ^{19}F NMR doublet (at 42.1 ppm, J = 10.8 Hz). However, this product could not be purified and analyzed adequately and its structure [perhaps 4-fluoropyrene (4)] has not been established. The melting point of 2 was practically identical with that reported in the literature.[16] The melting point of 3 (147–148°) was very similar to that reported by Jensen and Berg (151–152°).[17] The structures of 2 and 3 were supported also by the elemental analyses and the appropriate molecular ions in the mass spectra. The 1 isomer (2) has previously been prepared by the conventional Balz–Schieman method.[16] Very low yields of 2 (as a picrate) were obtained also by a direct fluorination of pyrene with *p*-tolyl iododifluoride.[16] The 2 isomer (3) has previously been prepared by the use of cine substitution via a 1,2-dehydropyrene intermediate: 1-bromopyrene was converted to a mixture of 1- and 2-aminopyrene, the amines were separated, and 2-aminopyrene was transformed by the Balz–Schieman method to 3.[17,18] The fluorination of pyrene with xenon difluoride yielded also appreciable amounts (ca. 25%) of "dimeric" products [$(C_{16}H_9)_2$, $C_{16}H_8F)_2$, $C_{16}H_8F$–$C_{16}H_9$ (?), prominent mass spectral signals at *m/e* 438, 420, and 402] which were not further characterized. It should be noted that comparable results were obtained in an open system and in a vacuum line system. Furthermore, the XeF_2/pyrene ratio did not affect the yields of the various substitution products of the reaction.

The mass spectra of some fractions obtained from the chromatography, including the impure 4-fluorination product, indicated the formation of difluoropyrene isomers, but these could not be separated and characterized. It has recently been reported that xenon difluoride adds fluorine to the phenanthrene system to form vicinal difluorides.[19]

The relative yields of 2 and 3 are exceptional, in view of the overwhelming preference of position 1 as the initial site of electrophilic substitutions of pyrene.[18,20–21] It may reflect the lower degree of selectivity of the attacking species.

The direct fluorination of pyrene with xenon difluoride widens the scope and generality of this fluoroaromatic syn-