(d, J = 22.5 Hz to d, J = 10 Hz, 3 F), −78.6 (m, 1 F), and −82.3 ppm (m, 1 F).

Anal. Calcd for $C_7H_2F_{10}N_2O$: C, 26.26; H, 0.65; F, 59.35; N, 8.75. Found: C, 26.49; H, 0.84; F, 58.82; N, 8.59.

Reaction of 18 with 2*H*-Hexafluoroisopropyl Alcohol.—A solution of 4.33 g (0.025 mol) of **18** in 10 ml of 2*H*-hexafluoroisopropyl alcohol was allowed to remain at room temperature for 5 days. The crystals that precipitated were collected on a filter and dried in air (4.04 g). A second crop was obtained by mixing the filtrate with water (3.22 g). The combined samples were recrystallized from benzene to give 5.3 g of 2,2,2-trifluoro-1-(trifluoromethyl)ethyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate as colorless crystals: mp 78–80°; ^{19}F nmr (CCl_3F) δ −69.1 (d, J = 21 Hz to d, J = 10 Hz, 3 F), −73.7 (d, J = 7 Hz, 6 F), −77.3 (m, 1 F), and −81.0 ppm (m, 1 F); ir (KBr) 5.70 μ (C=O).

Anal. Calcd for $C_7H_2F_{11}NO_2$: C, 24.65; H, 0.59; F, 61.27; N, 4.11. Found: C, 25.02; H, 0.81; F, 60.71; N, 4.60.

1-(*p*-Chlorophenyl)-3-(trifluorovinyl)urea.—A solution of 2.40 g (0.019 mol) of *p*-chloroaniline in 10 ml of ether was added dropwise to a stirred solution of 2.34 g (0.019 mol) of trifluorovinyl isocyanate in 25 ml of ether. The solid that precipitated was collected on a filter and washed with ether. There was obtained 3.77 g (80%) of the urea as colorless plates: mp 170–172° dec; ir (KBr) 3.02 (NH), 5.47 (CF_2=C), and 6.00 μ (C=O); ^{19}F nmr (acetone) δ −106.8 (d, J = 72 Hz to d, J = 44 Hz to m, 1 F), −118.5 (d, J = 72 Hz to d, J = 113 Hz to m, 1 F), and −127.7 ppm (d, J = 113 Hz to d, J = 44 Hz to m, 1 F).

Anal. Calcd for $C_9H_6ClF_3N_2O$: C, 43.13; H, 2.42; Cl, 14.15; F, 22.74; N, 11.18. Found: C, 43.24; H, 1.94; Cl, 14.01; F, 22.75; N, 10.86.

1-(*p*-Chlorophenyl)-3-(1,1,2,2,2-pentafluoroethyl)urea.—A solution of 2.54 g (0.02 mol) of *p*-chloroaniline in 25 ml of ether cooled to −50° was mixed with 3.22 g (0.02 mol) of pentafluoroethyl isocyanate. The reaction mixture was warmed to 25°, and the white solid that precipitated was collected on a filter, washed with cold ether, and dried to give 4.6 g of the urea as white crystals: mp 133–40° dec; ir (KBr) 5.98 μ (C=O); ^{19}F nmr (acetone) δ −79.4 (s, 2 F) and −87.4 ppm (s, 3 F).

Anal. Calcd for $C_9H_6ClF_5N_2O$: Cl, 12.29; F, 32.91; N, 9.71. Found: Cl, 12.83; F, 32.51; N, 9.51.

Methyl 1,2-Dichloro-2,2-difluoro-1-(trifluoromethyl)ethylcarbamate.—Methanol (4.1 ml, 0.1 mol) was added dropwise to a 24.4-g sample (0.1 mol) of 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate cooled in an ice bath. The reaction mixture solidified. Recrystallization from pentane gave 22.0 g (80%) of the carbamate as colorless crystals: mp 46–47°; ^{19}F nmr (CCl_3F) δ −62.0 (m, 2 F) and −72.1 ppm (d, J = 14 Hz to d, J = 12 Hz, 3 F); ir (KBr) 3.92 (NH), 5.64, and 5.73 μ (CO).

Anal. Calcd for $C_5H_4Cl_2F_5NO_2$: C, 21.76; H, 1.46; Cl, 25.69; F, 34.42; N, 5.07. Found: C, 22.17; H, 1.48; Cl, 25.27; F, 34.72; N, 4.79.

1-(*p*-Chlorophenyl)-3-(2-chloro-1,1,2,2-tetrafluoroethyl)urea.—A solution of 2.04 g (0.016 mol) of *p*-chloroaniline in 10 ml of ether was added dropwise to a solution of 2.85 g (0.016 mol) of 2-chloro-1,1,2,2-tetrafluoroethyl isocyanate in 25 ml of ether cooled to 0°. The precipitate that formed was collected on a filter, washed with cold ether, and dried in air to give 3.92 g (80% yield) of the urea as colorless crystals: mp 137–138° dec (gas); ir (KBr) 3.02 (NH), 5.97, 6.40, 6.24, and 6.68 μ; ^{19}F nmr (acetone) δ 71.5 (t, J = 8 Hz, 2 F) and −91.7 ppm (m, 2 F).

Anal. Calcd for $C_9H_5Cl_2F_4N_2O$: C, 35.43; H, 1.98; Cl, 23.24; F, 24.91; N, 9.19. Found: C, 35.56; H, 1.75; Cl, 23.22; F, 24.06; N, 8.97.

Registry No.—**1**, 667-49-2; **2**, 17773-81-8; **3**, 41594-54-1; **4**, 17773-79-4; **5**, 41594-56-3; **6**, 41594-24-5; **7**, 41594-57-4; **7** polymer, 41588-59-4; **8**, 356-74-1; **10**, 41594-59-6; **11**, 422-43-5; **12**, 41594-60-9; **13**, 41594-61-0; **14**, 710-53-2; **15**, 41594-63-2; **16**, 3749-02-8; **17**, 41594-65-4; **18**, 41594-66-5; **20**, 41594-67-6; **21**, 41594-68-7; **22**, 41594-69-8; tetraethylammonium azide, 993-20-4; hexafluoroacetone imine, 1645-75-6; 1-chloro-2,2,2-trifluoro-1-(trifluoromethyl)ethyl isocyanate, 39095-53-9; 1,2-dichloro-2,2-difluoro-1-(chlorodifluoromethyl)ethyl isocyanate, 41594-25-6; 1,3-dichlorotetrafluoroacetone imine, 1619-97-2; 1,2-dibromo-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate, 41594-27-8; 2,2,3,3,4,4-hexafluoro-1-(trifluoromethyl)-cyclobutylamine, 41594-28-9; methyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate, 41594-29-0; 1,3-bis[2,2-difluoro-1-(trifluoromethyl)vinyl]urea, 41594-30-3; 2*H*-hexafluoroisopropyl alcohol, 920-66-1; 2,2,2-trifluoro-1-(trifluoromethyl)ethyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate, 41594-32-5; 1-(*p*-chlorophenyl)-3-(trifluorovinyl)urea, 41594-33-6; *p*-chloroaniline, 106-47-8; 1-(*p*-chlorophenyl)-3-(1,1,2,2,2-pentafluoroethyl)-urea, 41594-34-7; methyl 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethylcarbamate, 41594-35-8; 1-(*p*-chlorophenyl)-3-(2-chloro-1,1,2,2-tetrafluoroethyl)urea, 41594-36-9.

syn-8,16-Difluoro[2.2]metacyclophane-1,9-diene[1]

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Normally, syntheses of metacyclophanes lead to the anti conformational isomer. In sharp contrast to this generalization, the condensation of 2,6-bis(bromomethyl)fluorobenzene (**3**) with sodium sulfide gives exclusively the syn isomer of 9,18-difluoro-2,11-dithia[3.3]metacyclophane (**4**) in 37% yield. When **4** is carried through the two-step reaction sequence of a Stevens rearrangement followed by a Hofmann elimination, the corresponding *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) is formed in good yield. Although **7** does not spontaneously undergo valence tautomerization to *cis*-15,16-difluorodihydropyrene (**10**), thermal rearrangement of **7** gives 1-fluoropyrene (**11**), suggesting the intervention of *cis*-15,16-difluorodihydropyrene (**10**) as a transient intermediate.

In previous publications we have indicated the synthetic utility of the two-step reaction sequence—Stevens rearrangement and Hofmann elimination—for transforming sulfide linkages to carbon–carbon double bonds.[2,3] This procedure has been especially useful for preparing derivatives of 15,16-dihydropyrene.[2] One of the striking features of such derivatives is their valence tautomerization, both thermally and photochemically, to the corresponding [2.2]metacyclophane-1,9-diene derivatives (**1** ⇌ **2**). Thus far this valence tautomerization has only been studied for examples where the substituents at the 15 and 16 positions are hydrogen or alkyl.[2,4,5] However, Schmidt, on the basis of an extended Hückel calculation, has made the theoretical prediction that in this valence tautomerization (**1** ⇌ **2**) the *trans*-15,16-dihydropyrene moiety **1** will be preferred for other substituents as well, namely fluoro.[6]

(1) We thank the National Science Foundation for their support of this investigation.

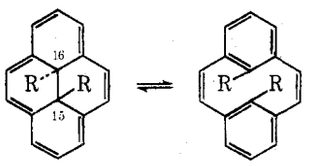
(2) R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970).

(3) V. Boekelheide and P. H. Anderson, *Tetrahedron Lett.*, 1207 (1970).

(4) V. Boekelheide and T. A. Hylton, *J. Amer. Chem. Soc.*, **92**, 3669 (1970).

(5) H.-R. Blattman and W. Schmidt, *Tetrahedron*, **26**, 5885 (1970).

(6) W. Schmidt, Doctoral Dissertation, Federal Institute of Technology, Zurich, 1970.



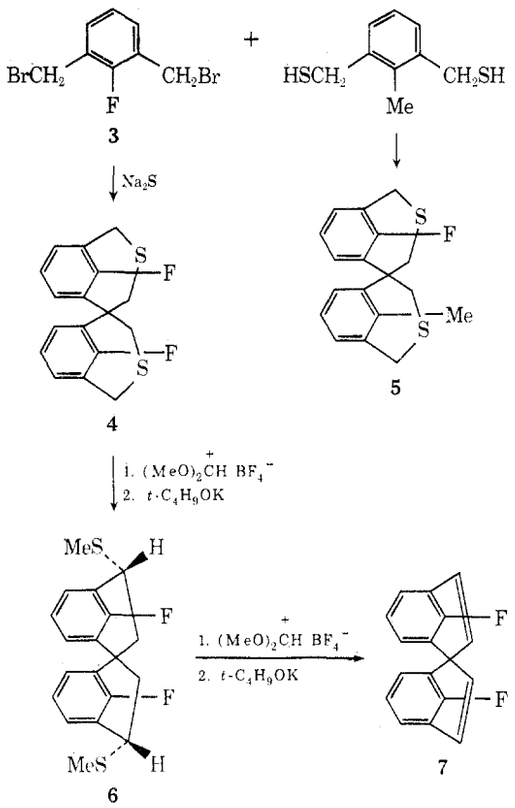
1 2

To test this prediction we undertook the synthesis of *anti*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**2**, R = F) following the general method developed for the corresponding dimethyl derivative (**2**, R = CH_3).[2]

Treatment of 2-fluoro-*m*-xylene with *N*-bromosuccinimide gave the necessary starting material, 2,6-bis(bromomethyl)fluorobenzene (**3**), in 41% yield. The reaction of **3** with sodium sulfide gave the corresponding 9,18-difluoro-2,11-dithia[3.3]metacyclophane (**4**) as the pure syn isomer in 37% yield. This is in sharp contrast to the corresponding methyl analog, where the ratio of syn to anti isomers formed is 1:7. Normally the anti isomer in the 2,11-dithia[3.3]metacyclophane series is appreciably more stable than the syn isomer. However, as Vögtle and Schunder have shown,[7] the signals of the methylene protons of **4** appear as an AB pattern which at 60 MHz coalesce at a temperature of 157° ($\Delta\nu$ = 65 Hz; $\Delta G^{\ddagger}_{157}$ = 21.1 kcal/mol). In the case of **4** the assignment of conformation is not obvious from its nmr spectrum and so we resorted to dipole moment measurements to answer the question. The anti conformation of **4** has a center of symmetry so that its dipole moment would be expected to be near zero. On the other hand, the syn conformer of **4** would be expected to have a sizable dipole moment comparable to fluorobenzene. The dipole moment of **4** was measured in benzene following the method of Smith[8a] and was found to be 1.26 D, clearly indicating it to be the syn conformer. For comparison the dipole moment of fluorobenzene is 1.46 D.[8b]

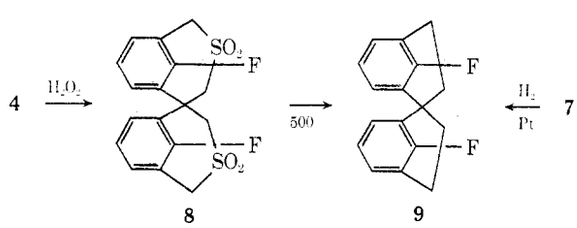
The reasons for the greater thermodynamic stability of the syn conformer of **4** compared to the anti are not clear, but it may be a result of the strong electrostatic repulsion involved in placing a fluorine atom over the aromatic π-electron cloud as is required in the anti conformer. To see whether a single fluoro substituent would still be effective in stabilizing the syn conformer, we prepared 8-fluoro-16-methyl-2,11-dithia[3.3]metacyclophane (**5**) by the condensation of 2,6-bis(mercaptomethyl)toluene with **3**. In this case **5** was formed with the ratio of syn to anti isomers being 3:2. Similar results have been reported by Vögtle and Neumann.[9] Even in this instance the repulsion of a single fluoro group apparently outweighs the greater strain energy associated with the syn conformation.

The important consequence of the formation of only the syn conformer of **4** was that we were in the wrong series, since syn conformers lead to *cis*-15,16-dihydropyrene derivatives rather than trans. However, in previous examples we had found that the Stevens rearrangement effected a major amount of isomerization from syn to anti conformation.[2] Therefore, we went ahead with the syn isomer. The Stevens rearrangement of **4** gave a mixture of isomers in about 50% yield. From this a pure crystalline isomer was isolated whose nmr spectrum is in accord with structure **6**. Further, measurement of the dipole moment of **6** gave a value of 1.66 D, confirming the syn conformation of the molecule.



3 4 5 6 7

Subjection of **6** to a Hofmann elimination then gave *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) in 80% yield. Again, the dipole moment found for **7** was 1.12 D, in agreement with the assigned syn conformation. Catalytic hydrogenation of **7** readily gave the corresponding *syn*-8,16-difluoro[2.2]metacyclophane (**9**). The synthesis of **9** can also be accomplished by oxidation of **4** to the bis(sulfone) **8** which, on pyrolysis at 500°, gives **9** in 64% yield.[10] Although the accepted mechanism for the pyrolysis of sulfones postulates that the reaction proceeds through an intermediate diradical, a diradical which in this case could isomerize to the anti conformation, we could find no evidence for the formation of the anti conformer in our pyrolysate.



4 8 9 7

Even though by the rule of conservation of orbital symmetry the concerted valence tautomerization of **7** to *cis*-15,16-difluorodihydropyrene (**10**) is an allowed process, there is no evidence for the occurrence of such a valence tautomerization of **7** at room temperature. When a sample of **7** was heated in a sealed tube at 120°, it was transformed into a fluoropyrene whose properties

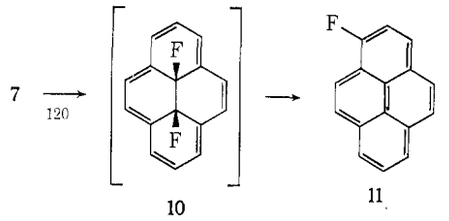
(7) F. Vögtle and L. Schunder, *Chem. Ber.*, **102**, 2677 (1969).

(8) (a) J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950); (b) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948).

(9) F. Vögtle and P. Neumann, *Tetrahedron*, **26**, 5299 (1970).

(10) F. Vögtle [*Angew. Chem.*, **81**, 258 (1969)] has also reported the pyrolysis of **8** to give **9**, but only in 15–20% yield.

are in accord with those recorded for 1-fluoropyrene (**11**).[11] Presumably, this thermal rearrangement and elimination involves **10** as a transient intermediate.



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Experimental Section[12]

2,6-Bis(bromomethyl)fluorobenzene (3).—A mixture of 62.1 g of 2-fluoro-*m*-xylene[13] and 178 g of *N*-bromosuccinimide in 900 ml of carbon tetrachloride containing a small quantity of benzoyl peroxide was boiled under reflux for 5 hr. After filtration, the filtrate was concentrated and the residual solid was recrystallized from cyclohexane to give 57.3 g (41%) of white crystals: mp 90.0–91.5°; nmr ($CDCl_3$), triplet at τ 2.72 (1 H, J = 6 Hz, ArH), a doublet at 2.94 (2 H, J = 6 Hz, ArH), and a singlet at 5.54 (4 H, $-CH_2$).

Anal. Calcd for $C_8H_7Br_2F$: C, 34.08; H, 2.50. Found: C, 33.98; H, 2.52.

***syn*-9,18-Difluoro-2,11-dithia[3.3]metacyclophane (4).**—A solution of 2.82 g of 2,6-bis(bromomethyl)fluorobenzene (**3**) in 100 ml of benzene and a solution of 2.40 g of sodium sulfide nonahydrate in 100 ml of 85% aqueous ethanol were added separately, but simultaneously, from two Hershberg funnels to 800 ml of boiling ethanol. When addition was complete (3.5 hr), the solution was concentrated. The residual solid was taken up in benzene and chromatographed over silica gel using a 25% benzene in petroleum ether (bp 30–60°) mixture for elution. The material from the main eluate fraction was recrystallized from carbon tetrachloride to give 575 mg (37%) of white crystals: mp 199–200°; uv (cyclohexane) 218 nm (ϵ 16,150), 242 (3700, sh), 261 (2440, sh), and 269 (2400); nmr ($CDCl_3$), a multiplet at τ 2.67–3.20 (6 H, ArH) and an AB quartet at 5.67 and 6.61 (8 H, J = 15 Hz, $-CH_2$); mass spectrum (70 eV) m/e (rel intensity) 308 (93), 185 (23), 154 (24), 123 (100), and 109 (33).

Anal. Calcd for $C_{16}H_{14}F_2S_2$: C, 62.31; H, 4.58. Found: C, 62.26; H, 4.52.

9-Fluoro-18-methyl-2,11-dithia[3.3]metacyclophane (5).—A solution of 2.82 g of 2,6-bis(bromomethyl)fluorobenzene (**3**) in 200 ml of benzene and a solution of 1.84 g of 2,6-bis(mercaptomethyl)-toluene[2] and 0.8 g of sodium hydroxide in 200 ml of 85% aqueous ethanol were added separately, but simultaneously, from two Hershberg funnels to 750 ml of boiling ethanol. When addition was complete (3.5 hr), the solution was concentrated. The residual solid was taken up in dichloromethane and washed successively with dilute aqueous acid, dilute aqueous base, and water. After the organic extract was dried and concentrated, the residual solid was chromatographed over silica gel using a 20% benzene in petroleum ether mixture for elution. The material from the main fraction of eluate was recrystallized from carbon tetrachloride to give 760 mg (25%) of white crystals; mp 200–205°; nmr ($CDCl_3$), a multiplet at τ 2.84–3.55 (6 H, ArH), a multiplet at 5.64–6.86 (8 H, $-CH_2$), a doublet at 7.59 (1.8 H, J = 2 Hz, $ArCH_3$), and a singlet at 8.51 (1,2 H, $ArCH_3$). The ratio of the integrated areas of the aromatic methyls at τ 7.59 and 8.51 is 3:2 and corresponds to the ratio of syn and anti conformers. Attempts to separate this mixture by further crystallization, column chromatography, or thin layer chromatography were to no avail.

Anal. Calcd for $C_{17}H_{17}FS_2$: C, 67.07; H, 5.63. Found: C, 66.83; H, 5.60.

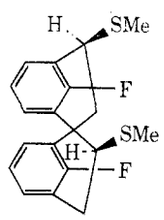
Bis(sulfonium) Fluoroborate of 4.—To a solution of 3.0 g of **4** in 150 ml of dichloromethane held at −78° was added with stirring 6.3 g of dimethoxycarbonium fluoroborate.[14] The mixture was then allowed to warm to room temperature and stirring was continued overnight. The solid precipitate was collected, triturated with ethyl acetate, and dried to give 5.0 g (100%) of a white solid. A portion was recrystallized from water to give white crystals, mp 220° dec.

Anal. Calcd for $C_{18}H_{20}B_2F_{10}S_2$: C, 42.21; H, 3.93. Found: C, 42.05; H, 4.01.

Stevens Rearrangement to Give 6.—To a solution of 4.19 g of potassium *tert*-butoxide in 200 ml of dry tetrahydrofuran there was added with stirring 4.90 g of the bis(sulfonium) fluoroborate of **4**. The mixture was stirred at room temperature under a nitrogen atmosphere for 9 hr. Then the mixture was diluted with 400 ml of dichloromethane, washed successively with dilute aqueous acid and water, and dried. Concentration gave 2.8 g of a yellow oil from which 710 mg of **6** separated as a crystalline solid. This, on recrystallization from cyclohexane, gave 690 mg (22%) of **6** as white crystals: mp 193.5–194°; uv (cyclohexane) 274 nm (ϵ 910) and 281 (830); nmr ($CDCl_3$), a multiplet at τ 2.22–2.44 (2 H, ArH next to $-CHSCH_3$), a multiplet at 2.57–2.80 (4 H, ArH), an ABC system at 6.08, 6.96, and 7.42 (6 H, J_{AB} = 4 Hz, J_{BC} = 12 Hz, J_{AC} = 11 Hz, $-CH-$ and $-CH_2$), and a singlet at 7.88 (6 H, $-SCH_3$); mass spectrum (70 eV) m/e (rel intensity) 336 (100), 288 (15), 221 (18), 202 (21), 169 (37), and 168 (16).

Anal. Calcd for $C_{18}H_{18}F_2S_2$: C, 64.25; H, 5.39. Found: C, 64.62; H, 5.57.

The mother liquor from which **6** crystallized was taken up in a 10% benzene in petroleum ether mixture and chromatographed over silica gel. The main fraction of eluate gave a second isomer, assigned structure **12** as shown below, as 800 mg (25%) of a color-



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less oil: nmr ($CDCl_3$), a multiplet at 3.0 (2 H, ArH *nearest* sulfur), a multiplet at 3.6 (4 H, ArH), an ABC system at 5.09, 6.19, and 7.88 (6 H, J_{AB} = 8 Hz, J_{BC} = 12 Hz, and J_{AC} = 8 Hz, $-CH-$ and $-CH_2-$), a singlet at 7.82 (6 H, $-SCH_3$); mass spectrum (70 eV) m/e (rel intensity) 336 (100), 288 (13), 221 (20), 202 (25), 169 (35), and 168 (15).

Anal. Calcd for $C_{18}H_{18}F_2S_2$: C, 64.25; H, 5.39. Found: C, 64.35; H, 5.61.

Bis(sulfonium) Fluoroborate of 6.—To a solution of 610 mg of **6** in 25 ml of dichloromethane held at −78° was added 730 mg of dimethoxycarbonium fluoroborate with stirring. The mixture was allowed to warm and was then stirred overnight at room temperature. The crystalline precipitate was collected, triturated with ethyl acetate, and dried. This gave 770 mg (95%) of a white solid, of which a portion was recrystallized from water to give white crystals, mp 290° dec.

Anal. Calcd for $C_{20}H_{24}B_2F_{10}S_2$: C, 44.47; H, 4.48. Found: C, 44.33; H, 4.47.

***syn*-8,16-Difluoro[2.2]metacyclophane-1,9-diene (7).**—To a solution of 750 mg of potassium *tert*-butoxide in 125 ml of dry tetrahydrofuran there was added 740 mg of the bis(sulfonium) fluoroborate of **6**. After the mixture had been stirred for 2 hr at room temperature, it was diluted with 200 ml of dichloromethane and washed successively with dilute aqueous acid and water. The organic extract was then dried and concentrated. The residual solid was taken up in petroleum ether and chromatographed over silica gel. The material from the main fraction of eluate was recrystallized from a dichloromethane–cyclohexane mixture to give 260 mg (80%) of white crystals: mp 89° dec; uv (cyclohexane) 278 nm (ϵ 3300) and 337 (830); nmr ($CDCl_3$), a multiplet at τ 2.86–3.18 (6 H, ArH) and a singlet at 3.59 (4 H, $-CH{=}CH-$); fluorine nmr (acetone-d_6) signal at +93 ppm relative to $CFCl_3$ as an internal standard; mass spectrum (70 eV) m/e (rel intensity) 240 (47), 239 (49), 238 (27), 221 (33), 220 (100), 202 (15), and 110 (20).

(11) P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4486 (1955).

(12) Elemental and mass spectral analyses were determined by Dr. S. Rottschaefer, University of Oregon Microanalytical Laboratories. Infrared spectra were measured with a Beckman IR-5a; visible and ultraviolet spectra with a Cary 15; nmr spectra with a Varian A-60 or HA-100 spectrometer; and mass spectra with a Consolidated Model 21-110 spectrometer.

(13) R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).

(14) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

Anal. Calcd for $C_{16}H_{10}F_2$: C, 79.99; H, 4.19. Found: C, 79.85; H, 4.16.

When compound **12**, isomeric to **6**, was converted to the corresponding bis(sulfonium) fluoroborate and subjected to the same conditions for the Hofmann elimination, as described above for the preparation of **7**, the reaction mixture became a deep green but turned colorless during work-up. The material isolated was a complex mixture whose nmr spectrum suggested the presence of pyrene and fluoropyrene derivatives.

Bis(sulfone) 8.—A mixture of 25 mg of **7** in 10 mg of glacial acetic acid containing 1 ml of 30% aqueous hydrogen peroxide was boiled under reflux for 24 hr. When the solution was allowed to cool, a crystalline solid separated. This was collected, washed with methanol, and dried to give 30 mg (100%) of a white powder: mp >350°; nmr ($AsCl_3$), a multiplet at τ 2.68 (4 H, ArH), a triplet at 3.15 (2 H, ArH), and an AB quartet at 5.52 and 5.94 (8 H, J = 14 Hz, $-CH_2SO_2-$).

Anal. Calcd for $C_{16}H_{14}O_4F_2S_2$: C, 51.60; H, 3.79. Found: C, 51.56; H, 3.75.

Pyrolysis of 8 to Give 9.—The bis(sulfone) **8** (75 mg) was placed in a pyrolysis flow system modeled after that described by Haenel and Staab.[15] The first furnace was at 340° and the second at 500° with the pyrolysis requiring 12 hr. The solid pyrolysate was recrystallized from cyclohexane to give 31 mg (64%) of white crystals: mp 156–158°; uv (cyclohexane) 272 nm (ϵ 700) and 279 (600); nmr ($CDCl_3$), a multiplet at τ 2.78–3.10 (6 H, ArH) and a multiplet at 7.26 (8 H, $-CH_2$); fluorine nmr (acetone-d_6) signal at +123.1 ppm relative to $CFCl_3$ as an internal standard; mass spectrum (70 eV) m/e (rel intensity) 244 (100), 224 (24), 223 (19), 203 (16), 202 (10), 201 (23), and 122 (32).

(15) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970).

Anal. Calcd for $C_{16}H_{14}F_2$: mol wt, 244.106. Found (high-resolution mass spectrometry): mol wt, 244.104 ± 0.01.

Hydrogenation of 7 to Give 9.—A mixture of 9 mg of *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) and 15 mg of a prereduced platinum catalyst in 5 ml of ethyl acetate was subjected to hydrogenation at room temperature and atmospheric pressure. After removal of the catalyst and solvent, the residual solid was recrystallized from cyclohexane to give white crystals, mp 156–158°, identical in all respects with the sample of **9** described previously.

Thermolysis of *syn*-8,16-Difluoro[2.2]metacyclophane-1,9-diene (7) to Give 1-Fluoropyrene (11).—A solution of 40 mg of *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) in 5 ml of dry tetrahydrofuran was carefully degassed and sealed in a pyrolysis tube. This was then heated at 120° for 68 hr. The tube was then opened and the contents were concentrated to give a crystalline solid. This was taken up in petroleum ether and chromatographed over silica gel to give 36 mg (98%) of white crystals, mp 136.5–138.0°, nmr ($CDCl_3$), a multiplet at τ 1.8–2.52.

Anal. Calcd for $C_{16}H_9F$: mol wt, 220.069. Found (high-resolution mass spectrometry): 220.067 ± 0.01.

The picrate derived from this material melted at 207–209° [Bavin and Dewar[11] give 135–136° for the melting point of 1-fluoropyrene (**11**) and 208–210° for the melting point of the corresponding picrate].

Registry No.—**3**, 25006-86-4; **4**, 25117-62-8; **4** bis(sulfonium) fluoroborate, 41560-37-6; **5**, 30736-36-8; **6**, 41563-60-4; **6** bis(sulfonium) fluoroborate, 41560-38-7; **7**, 41563-61-5; **8**, 41563-62-6; **9**, 22506-31-6; **11**, 1691-65-2; **12**, 41563-65-9; 2-fluoro-*m*-xylene, 443-88-9; *N*-bromosuccinimide, 128-08-5; 2,6-bis(mercaptomethyl)toluene, 41563-67-1; dimethoxycarbonium fluoroborate, 18346-68-4; potassium *tert*-butoxide, 865-47-4.

Attempted Syntheses of *trans*-15-Methyl-15,16-dihydropyrene[1]

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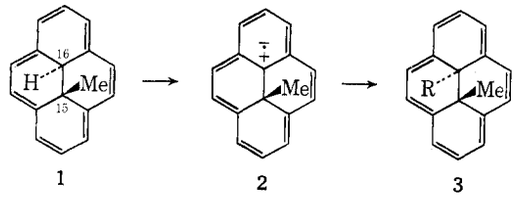
A possible synthesis of the potentially interesting *trans*-15-methyl-15,16-dihydropyrene (**1**) has been investigated by subjecting *anti*-9-methyl-2,11-dithia[3.3]metacyclophane to the two-step reaction sequence of a Stevens rearrangement and a Hofmann elimination. However, the only product isolated was pyrene. When the Hofmann elimination was conducted using a high vacuum train, the green mixture could be shown to contain radicals by esr measurements, and the loss of color accompanying the formation of pyrene resulted in evolution of methane, as shown by mass spectroscopy. Alternatively, the possible photoisomerization of 8-methyl[2.2]metaparacyclophane-1,9-diene (**18**) to **1** was attempted without success, even though the photoisomerization of 8-methyl[2.2]metaparacyclophane (**19**) to 8-methyl[2.2]metacyclophane (**21**) occurs smoothly and in good yield.

Theoretically, *trans*-15-methyl-15,16-dihydropyrene (**1**) is a molecule of high interest because of its possible conversion to the corresponding radical or ions (**2**). Not only would these species be of inherent interest for examination of their physical properties, but they could be valuable synthetic intermediates for preparing dihydropyrenes with substituents at the 16 position as shown by **3**. For these reasons we have studied several



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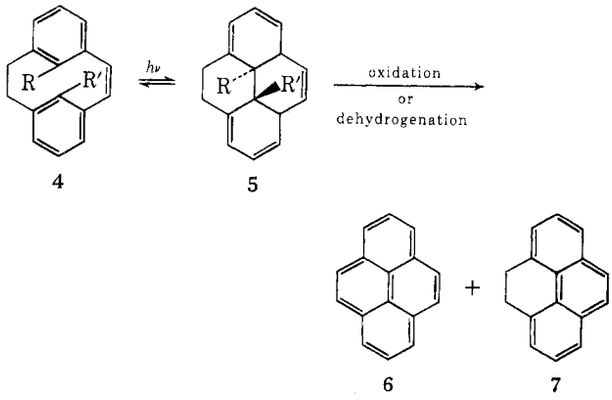
possible approaches which might lead to a synthesis of *trans*-15-methyl-15,16-dihydropyrene (**1**).

In an earlier study,[2,3] we had shown that [2,2]-metacyclophan-1-enes (**4**) are readily photoisomerized to the corresponding 4,5,15,16-tetrahydropyrenes (**5**). With both of the internal substituents being methyl (R = R′ = Me), dehydrogenation of **5** proceeded smoothly to give *trans*-15,16-dimethyldihydropyrene.



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(1) We thank the National Science Foundation for their support of this investigation.

(2) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3675 (1970).

(3) C. E. Ramey and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3681 (1970).