158. Preparation of 3,4-Fused Cyclopropabenzenes and Cyclopropabenzenyl Cations

by **Paul Müller*** and **Domingo Rodriguez**

Département de Chimie Organique, Université de Genève, CH–1211 Genève 4

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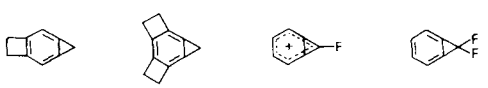
A series of 3,4-disubstituted (**4a, b**) or 3,4-fused (**4c–e**) 1,1-di-fluorocyclopropabenzenes, including the very strained 1,1-difluoro-3,4-dihydro-1*H*-cyclobuta[*a*]cyclopropa[*d*]benzene (**4e**) have been synthesized and characterized. Dissolution of these difluoro derivatives in fluorosulfonic acid affords the fluoro cations **3a–e**. ^{1}H-, ^{19}F-, and ^{13}C-NMR data of the cations are reported and discussed with respect to those of the precursors.

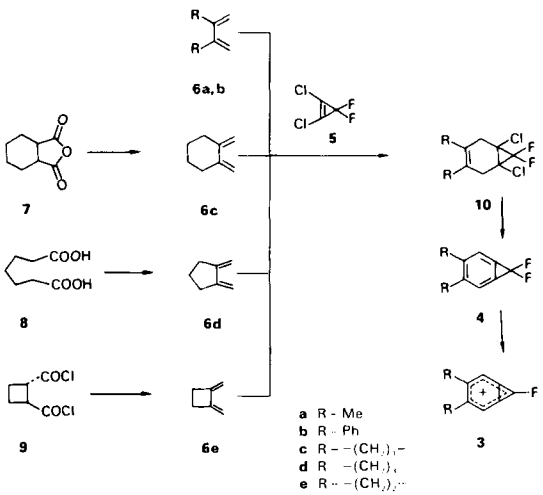
Introduction. – The chemistry of cyclopropabenzenes, the most highly strained members of the *o*-fused cycloalkabenzene series is now well established [1]. Recently, even more strained derivatives have been synthesized by fusion of cyclopropabenzenes to a second or third carbocyclic system, for example cyclobuta[*a*]cyclopropa[*d*]benzene **1** [2] and dicyclobuta[*a, c*]cyclopropa[*e*]benzene **2** [3]. In parallel, several halogen-stabilized cyclopropabenzenyl cations such as **3'** have been prepared by ionization of the corresponding difluoro precursors such as **4'** and characterized by ^{1}H-, ^{19}F-, and ^{13}C-NMR



1 **2** **3'** **4'**

data [4] [5]. Cyclopropabenzenyl cations are related to the aromatic tropylium ion [6] of which they represent the 1,3-didehydro derivatives. Alternatively, they may be viewed as benzo-annelated cyclopropenyl cations [7]. Their high degree of stabilization by π-electron delocalization has been recognized as early as 1952 [8]. However, this favorable effect is compensated by steric strain in the σ skeleton because of 'inverted geometry' at the positions of ring junction. It is this balance of electronic stabilization and strain which spurred our interest in cyclopropabenzenyl cations. The successful syntheses of **1** and **2** suggested that their 1,1-difluoro derivatives might be accessible and serve as precursors for fused cyclopropabenzenyl cations. In view of the reported instability of 1,1-difluorodicyclohexacyclopropabenzene [9], we investigated first the synthetic accessibility of 3,4-fused 1,1-difluorocyclopropabenzenes **4c–e** increasing the additional strain within the series by fusion with a cyclohexane, cyclopentane, and cyclobutane ring. In this communication, we report the synthesis of these compounds and their ionization to the 1-fluorocyclopropabenzenyl cations **3c–e**. The 3,4-dimethyl and 3,4-diphenyl derivatives **4a** and **4b** were synthesized for reference purposes and equally converted to the cations **3a** and **3b**, respectively.

Scheme



Syntheses. – The synthetic scheme used in all cases consists in *Diels-Alder* addition of 1,2-dichloro-3,3-difluorocyclopropene (**5**) to the appropriate butadiene **6** *(Scheme)*. The 2,3-dimethyl- and 2,3-diphenylbuta-1,3-dienes (**6a** and **6b**, resp.) are commercially available. Dienes **6c–e** were obtained by methods discussed in the literature.

The 1,2-dimethylidenecyclohexane (**6c**) was synthesized from cyclohexane-1,2-dicarboxylic anhydride (**7**) *via* reduction to the diol with $LiAlH_4$ [10]. The latter was converted to the dimesylate [10], and elimination with *t*-BuOK in DMSO [11] gave **6c** [12]. For the synthesis of 1,2-dimethylidenecyclopentane (**6d**) in 7 steps from pimelic acid (**8**), the latter was converted to the α'-dibromo ester *via Hell-Volhard-Zelinsky* bromination [13]. The α,α'-dibromo ester was cyclized (NaH) [14], and the resulting cyclopentene diester reduced by catalytic hydrogenation [14]. The ester groups were converted to quaternary ammonium salts by sussessive reaction with $LiAlH_4$ [10], PBr_3 [15], Me_3N [15], and $AgNO_3$/KOH. Pyrolysis at 120° [16] of the hydroxide afforded **6d** [17]. For the synthesis of 1,2-dimethylidenecyclobutane (**6e**), commercial *trans*-cyclobutane-1,2-dicarbonyl chloride (**9**) was converted to the diamine by reaction with Me_2NH [18] and $LiAlH_4$ [19]. The diamine was oxidized to the di-*N*-oxide and pyrolyzed [16] to furnish diene **6d** [17] [20][1]).

Diels-Alder addition of 1,2-dichloro-3,3-difluorocyclopropene [22] (**5**) to the dienes at 100° in presence of $NaHCO_3$ and hydroquinone afforded the substituted 1,6-dichloro-7,7-difluorobicyclo[4.1.0]hept-3-enes **10a–e** in 55–100% yield. Their ^{19}F-NMR data are collected in *Table 1*.

The *cis*/*trans* assignment of the F relative to the Cl substituents at the cyclopropane moiety of **10** was made on the grounds of analogies with other *Diels-Alder* adducts of **5** to 1,3-dienes [23]. The *cis*-substituent F_A resonates in the range of 30–35 ppm downfield from C_6F_6 and shows coupling with the CH_2 protons in the order of *ca.* 5 and 2 Hz. The *trans*-substituent F_M is found between 16 and 20 ppm, and H,F coupling is weak (unresolved).

Aromatization of the cycloadducts with *t*-BuOK in THF at low temperature, followed by anhydrous workup proceeded without difficulties, and even the most highly strained member of the series (**4e**) could be isolated and purified, despite of its tendency for rapid hydrolysis. The cyclopropabenzenyl cations **3a–e** formed upon dissolution of the difluoro precursors in cooled fluorosulfonic acid. The solutions were stored in sealed ampoules in liquid N_2 without decomposition for several weeks.

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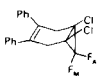
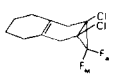
[1]) The syntheses of **6c–e** are described in detail in the Ph.D. thesis of *D.R.* [21].

Table 1. *^{19}F-NMR (C_6F_6) of 1,6-Dichloro-7,7-difluorobicyclo[4.1.0]hept-3-enes* **10**[a])

Compound	δ of center of *AM* system	δ_A	δ_M	$^2J(A,M)$
 **10′**	25.8	32.2 (*dtm*, ^4J(H,F) = 4 Hz)	19.4 (*d* br. *s*)	156
 **10a**	24.48	31.58 (*dm*)	17.38 (*d* br. *s*)	153
 **10b**	26.76	33.35 (*dtt*, ^4J(H,F) = 6, ^4J(H,F) = 1.8)	20.17 (*dm*)	154
 **10c**	24.55	31.64 (*dtt*, ^4J(H,F) = 5.2, ^4J(H,F) = 2.5)	17.47 (*d* br. *s*)	153
 **10d**	23.55	30.23 (*dtt*, ^4J(H,F) = 4.6, ^4J(H,F) = 2.3)	16.86 (*d* br. *s*)	155
 **10e**	23.13	29.65 (*dtt*, ^4J(H,F) = 4.1, ^4J(H,F) = 2.0)	16.60 (*d* br. *s*)	156

[a]) Chemical shifts in ppm relative to C_6F_6 (= 0 ppm); coupling constants *J* in Hz.

NMR Spectra of Fused 1,1-Difluorocyclopropabenzenes 4 and 1-Fluorocyclopropabenzenyl Cations 3. – The ^{1}H- and ^{13}C-NMR spectra of **3** and **4** were readily assigned upon comparison with the spectra of unsubstituted and 2,5-disubstituted compounds [4] [24]. Details are summarized in *Tables 3* and *4 (Exper. Part)*.

Fig. 1 shows the ^{13}C-NMR lines of the neutral precursors **4**. As expected, the effect of additional strain by ring fusion appears primarily at C(3)/C(4)[2]), whereas C(2)/C(5) is shifted upfield in the series by *ca.* 6 ppm, giving the lowest δ value for the cyclobuta derivative **4e** (109.6). This latter value corresponds to that in the parent cyclobutacyclopropabenzene **1** (110.0 ppm [25]). The insensitivity of C(2)/C(5) towards F substitution at C(1) is remarkable when compared to the shift of *ca.* 7 ppm for C(3)/C(4) in going from **1** to **4e**. The ^{13}C,H coupling constants at C(2)/C(5) vary in the series from **4a** (170 Hz) and **4c** (170) to **4d** (172) and **4e** (175 Hz); the value of **1** is 169 Hz [25]. By comparison, the ^{13}C,H coupling constant of the corresponding symmetrical dicyclobuta[*a,d*]benzene is 159.9 Hz [26] at the aromatic C–H bond, while the corresponding values for cyclopropabenzene are 168.5 (C(2)/C(5)) and 159.0 (C(3)/C(4)), which are shifted to 175 and 161 Hz in **4′** [24]. The change upon difluoro substitution at C(1) in **4′** is thus about the same as that in going from **1** to **4e**.

In the cations **3**, the ^{1}H-NMR lines of the protons at C(2)/C(5) are shifted downfield by 0.74–0.92 ppm, and those of the F substituents by 7.3–12.2 ppm as compared with the values of **4**. The ^{13}C-NMR lines are summarized in *Fig. 2*. The most intriguing feature is the very low sensitivity of C(2)/C(5) towards ionization; indeed, the downfield shift for C(2)/C(5) is only 0.3–1.1 ppm *(Table 2)*, but it amounts to *ca.* 40 for C(1), 10 for C(1a)/C(5a), and 25–30 for C(3)/C(4).

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[2]) For convenience, the arbitrary numbering depicted in *Figs. 1* and *2* was chosen for all compounds of type **3** and **4**. Systematic names are given in the *Exper. Part*.

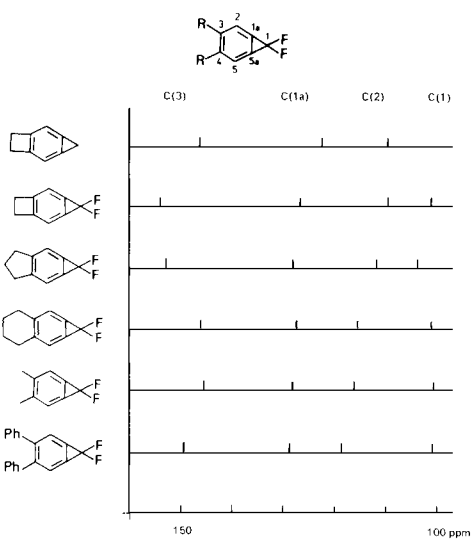

Fig. 1. *^{13}C-NMR shifts of 1,1-difluorocyclopropabenzenes* **4** (see also *Table 3, Exper. Part*)

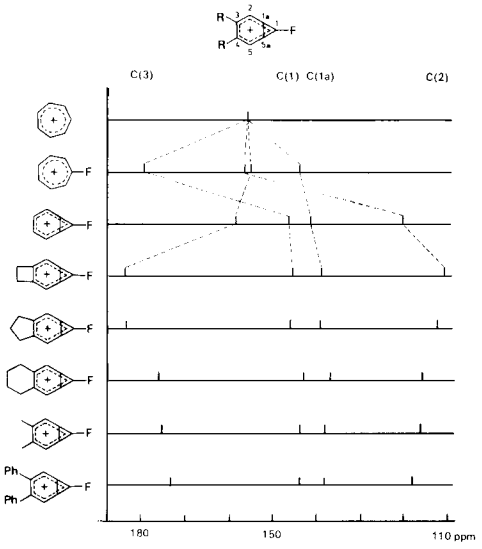

Fig. 2. *^{13}C-NMR shifts of 1-fluorocyclopropabenzenyl cations* **3** *and related compounds* (see also *Table 4, Exper. Part*)

Table 2. *NMR Downfield Shifts* [ppm] *for 1-Fluorocyclopropabenzenyl Cations* **3** vs. *1,1-Difluoro Precursors* **4**[a])[2])

	$\Delta\delta$ in ^{1}H-NMR H–C(2)/ H–C(5)	$\Delta\delta$ in ^{19}F-NMR F–C(1)	$\Delta\delta$ in ^{13}C-NMR C(1)	C(1a)/C(5a)	C(2)/C(5)	C(3)/C(4)	Δ^2J^{13} for H–C(2)/H–C(5) [Hz]
3′ *vs.* **4′**	0.66	20.0	47.8	11.6	3.8	23.6	20
3a *vs.* **4a**	0.92	7.3	41.8	9.8	0.3	29.7	19
3b *vs.* **4b**	0.77	12.0	42.6	9.3	0.4	24.3	–
3c *vs.* **4c**	0.74	12.2	41.8	9.4	0.3	29.6	19
3d *vs.* **4d**	0.95	8.6	42.0	10.6	0.5	30.0	19
3e *vs.* **4e**	0.86	10.0	43.5	11.8	1.1	29.0	20

[a]) Spectra measured in FSO_3D under Ar at $-40°$ (cations) and $CDCl_3$ (neutrals) (see *Exper Part*).

The observed ^{13}C-NMR data are in contradiction to various charge-density calculations: CNDO/S calculations [28] give rather similar charge densities for C(2)/C(5) and C(3)/C(4) in the 1-fluorocyclopropabenzenium cation **3′**, and these results are corroborated by MINDO/3 [29] and SCC-EH [30] (unsubstituted cations) treatments. It has been suggested that the reason for the anomalies should lie in the presence of the F substituent, but this seems less likely in view of the observation that in the case of the fluorotropylium ion, the MINDO/3 charge densities correlate well with the ^{13}C-NMR chemical shifts [31]. *Fig. 2* shows that the shift changes occurring upon introduction of the F substituent in the tropylium ion are less important than those due to the 1a,5a-bridging in **3′**. The effects due to fusion of an additional ring is disappointingly small, leading to the same trends as in the neutral precursors **4** (the C(3)/C(4) resonance lines move downfield by *ca.* 10 ppm in going from **3a** to **3e**, while the lines of C(2)/C(5) move upfield by 8 ppm; not unexpectedly, C(1) and C(1a)/C(5a) are least affected).

The relationship between ^{13}C-NMR chemical shift and charge-density has been postulated already in 1961 [32] and discussed repeatedly since [33]. On the other hand, it was recognized quite early that 'quantitative interpretations of ^{13}C-NMR chemical shifts should be made cautiously' [34]. In the case of cyclopropabenzenyl cations, it appears unwise to attempt a detailed interpretation as long as the unsubstituted ion is not available.

The magnitude of the ^{13}C,H coupling constant is related to geometric effects and electron demand in cations [35]. As in the neutral precursors, J(C,H) increases from **3a** (189), **3c** (189), **3d** (191), and **3e** (193), but ΔJ for ionization is almost constant *(Table 2)*.

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Experimental Part

General. See [36].

***Diels-Alder* Addition of Dienes 6 to 1,2-Dichloro-3,3-difluorocyclopropene (5).** – *1,6-Dichloro-7,7-difluoro-3,4-dimethylbicyclo[4.1.0]hept-3-ene* (**10a**). A soln. of 2,3-dimethylbuta-1,3-diene (**6a**; 1.64 g, 20 mmol) and **5** (1.45 g, 10 mmol) in CCl_4 (25 ml) containing 50 mg of $NaHCO_3$ and 50 mg of hydroquinone was heated in a sealed *Pyrex* tube to 100° during 24 h. After filtration, the solvent and excess **6a** were evaporated. The crude product was distilled in a bulb tube (60°/0.2 Torr) to give **10a** (1.87 g, 82%), m.p. 37–38°. IR ($CHCl_3$): 2920*w*, 2880*m*, 1450*m*, 1410*m*, 1250*m*, 1200*s*, 1175*m*, 1120*m*, 970*m*, 820*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.82 (*m*, 4H); 1.62 (*t*, J = 0.9, 6H). ^{13}C-NMR ($CDCl_3$): 107.7 (*dd*, ^1J(C,F) = 313.0, ^1J(C,F) = 294); 47.6 (*dd*, ^2J(C,F) = 12.0, ^2J(C,F) = 9.0); 36.8 (*dd*, ^3J(C,F) = 3, ^3J(C,F) = 2); 121.7 (*d*, ^4J(C,F) = 2.9); 18.3. ^{19}F-NMR: *Table 1*. MS: 230–226 (8, M^+), 191 (39), 175 (23), 155 (100), 141 (44), 115 (10), 105 (7), 91 (7), 77 (11), 65 (5), 51 (5).

1,6-Dichloro-7,7-difluoro-3,4-diphenylbicyclo[4.1.0]hept-3-ene (**10b**). For 8 d, 2,3-diphenylbuta-1,3-diene (**6b**; 0.62 g, 3 mmol) and **5** (1.9 g, 13 mmol) were heated to 100° in presence of 50 mg of $NaHCO_3$ and 50 mg of hydroquinone in 25 ml of CCl_4. The crude product was purified by column chromatography using silica gel and CH_2Cl_2 and subsequent fractional sublimation (80°/0.3 Torr): 0.55 g (52%) of **10b**, m.p. 90–92°. IR ($CHCl_3$): 3160*w*, 3060*w*, 3030*w*, 2980*w*, 2820*w*, 1600*w*, 1500*m*, 1460*m*, 1420*m*, 1260*m*, 1240*m*, 1200*m*, 1140*w*, 1110*m*, 990*m*, 830*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.5–7.3 (*m*, 2H); 7.2 (*m*, 4H); 6.95 (*m*, 4H); 3.40 (*m*, 4H). ^{13}C-NMR ($CDCl_3$): 107.7 (*dd*, ^1J(C,F) = 315.0, ^1J(C,F) = 296.7); 48.2 (*dd*, ^2J(C,F) = 11.6, ^2J(C,F) = 9.3); 37.2 (*t*, ^3J(C,F) = 2.4); 131.1 (*d*, ^4J(C,F) = 2.1); 140.5, 128.7, 128.0, 126.9. ^{19}F-NMR: *Table 1*. MS: 354–350 (10, M^+), 315 (11), 279 (16), 259 (20), 228 (12), 203 (21), 178 (34), 167 (19), 127 (28), 91 (100), 77 (13).

*1a,7a-Dichloro-1,1-difluoro-1a,2,3,4,5,6,7,7a-octahydro-1*H*-cyclohexa[*a*]cyclopropa[*d*]benzene* (**10c**). As for **10a** from 8.25 mmol of **5** and 9.26 mmol of **6c** [21]. Purification of the crude product by column chromatography with silica gel and CH_2Cl_2 afforded 1.75 g of **10c** (84%) which solidified at −10°. IR ($CHCl_3$): 2940*s*, 2840*s*, 1455*s*, 1420*s*, 1240*m*, 1200*s*, 1150*m*, 980*s*, 800*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.80 (*m*, 4H); 1.85 (*m*, 4H); 1.60 (*m*, 4H). ^{13}C-NMR ($CDCl_3$): 108.8 (*dd*, ^1J(C,F) = 312.5, ^1J(C,F) = 295.3); 48.6 (*dd*, ^2J(C,F) = 12.7, ^2J(C,F) = 9.6); 36.9 (*dd*, ^3J(C,F) = 3.0, ^3J(C,F) = 2.0); 125.2 (*d*, ^3J(C,F) = 2.1); 30.3; 23.6. ^{19}F-NMR: *Table 1*.

*1a,6a-Dichloro-1,1-difluoro-2,3,4,5,6,6a-hexahydro-1*H,*1a*H*-cyclopenta[*a*]cyclopropa[*d*]benzene* (**10d**). As for **10a** with **5** (1.5 g, 10.3 mmol) and **6d** [21] (1.0 g, 10.6 mmol): 1.5 g (61%) of **10d**. IR ($CHCl_3$): 2960*m*, 2900*s*, 2880*m*, 2850*s*, 1460*vs*, 1420*s*, 1330*m*, 1240*s*, 1210*s*, 1190*s*, 1150*m*, 1110*s*, 1050*m*, 980*s*, 810*s*. ^{1}H-NMR ($CDCl_3$): 2.85 (*m*, 4H); 2.25 (*m*, 4H); 1.85 (*m*, 2H). ^{13}C-NMR ($CDCl_3$): 108.6 (*dd*, ^1J(C,F) = 310.5, ^1J(C,F) = 296.4); 48.7 (*dd*, ^3J(C,F) = 13.0, ^2J(C,F) = 8.8); 32.7 (*dd*, ^3J(C,F) = 2.8, ^3J(C,F) = 2.1); 130.7 (*d*, ^3J(C,F) = 3.1); 36.2; 22.5. ^{19}F-NMR: *Table 1*. MS: 242–238 (19, M^+), 203 (100), 175 (26), 167 (98), 153 (27), 147 (25), 127 (29), 115 (19), 101 (10), 91 (24), 77 (17), 63 (17), 51 (23).

*1a,5a-Dichloro-1,1-difluoro-1a,2,3,4,5,5a-hexahydro-1*H*-cyclobuta[*a*]cyclopropa[*d*]benzene* (**10e**). As for **10a** with **5** (2.25 g, 15.5 mmol) and **6e** [21] (1.0 g, 12.5 mmol): 1.6 g (57%) of **10e**, after chromatography on silica gel with CH_2Cl_2. M.p. 36°. IR ($CHCl_3$): 2960*m*, 2920*s*, 1450*s*, 1410*s*, 1240*s*, 1190*s*, 1100*m*, 980*s*, 820*m*. ^{1}H-NMR

($CDCl_3$, 200 MHz): 2.85 (*m*, 4H); 2.45 (*m*, 4H). ^{13}C-NMR ($CDCl_3$): 107.8 (*dd*, ^1J(C,F) = 308.2, ^1J(C,F) = 298.8); 47.1 (*dd*, ^2J(C,F) = 13.3, ^2J(C,F) = 9.6); 30.6 (*dd*, ^3J(C,F) = 3.4, ^3J(C,F) = 1.7); 135.2 (*d*, ^4J(C,F) = 3.1); 29.9. ^{19}F-NMR: *Table 1*. MS: 228–224 (15, M^+), 191 (33), 189 (98), 175 (20), 161 (41), 153 (100), 133 (65), 127 (40), 113 (26), 103 (45), 91 (19), 77 (56), 63 (20), 51 (67).

Bis-dehydrohalogenation of 10a–e. – *1,1-Difluoro-3,4-dimethyl-1*H*-cyclopropabenzene* (**4a**). To a soln. of **10a** (0.23 g, 1 mmol) in dry THF (10 ml) was added at − 78° within 10 min sublimed *t*-BuOK (0.45 g, 4 mmol) in THF (10 ml). The brown mixture was stirred at − 78° (2 h), then warmed to r.t. The solvent was evaporated at 20°/100 Torr and the residue extracted with pentane. The insoluble salts were separated by filtration. After evaporation and bulb-to-bulb distillation (20°/0.05 Torr), **4a** was obtained (0.12 g, 78%) as colorless liquid. IR ($CHCl_3$): 3060*w*, 2980*m*, 2960*m*, 1705*m*, 1660*s*, 1465*s*, 1420*s*, 1390*s*, 1330*s*, 1230*s*, 1180 (br.), 1050 (br.), 990*m*, 850*m*. UV (hexane): 272 (3.20), 266 (3.27), 259 (3.14), 211 (3.78), 200 (3.73). ^{1}H-NMR (CDCl, 200 MHz): 7.31 (*t*, ^4J(H,F) = 4, 2H); 2.40 (*t*, ^6J(H,F) = 1, 6H). ^{13}C-NMR: *Table 3*. ^{19}F-NMR ($CDCl_3$): 83.5 (*tq* (apparent), ^4J(H,F) = 4, ^6J(H,F) = 1.2). MS: 154 (100, M^+), 133 (34), 127 (30), 119 (9), 103 (15), 99 (6), 77 (12), 63 (14), 51 (14).

*1,1-Difluoro-3,4-diphenyl-1*H*-cyclopropabenzene* (**4b**). As for **4a** with **10b** (0.15 g, 0.43 mmol). Sublimation (70°/0.03 Torr) of the crude product gave 0.07 g (58%) of **4b**, m.p. 100–102°. UV (hexane): 277 (3.66), 238 (4.21), 213 (4.42), 201 (4.15). IR ($CHCl_3$): 3000*w*, 3040*w*, 1650*m*, 1440*w*, 1410*m*, 1310*w*, 1290*m*, 1210*w*, 1180*s*, 1050 (br.), 870*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.57 (*t*, ^4J(C,F) = 3.8); 7.23 (*m*, 6H); 7.10 (*m*, 4H). ^{13}C-NMR: *Table 3*. ^{19}F-NMR ($CDCl_3$): 82.2 (*t*, ^4J(H,F) = 4, 2F). MS: 278 (74, M^+), 258 (30), 221 (22), 206 (81), 205 (52), 191 (26), 134 (100), 91 (52), 77 (26), 65 (13), 51 (15).

*1,1-Difluoro-3,4,5,6-tetrahydro-1*H*-cyclohexa[*a*]cyclopropa[*d*]benzene* (**4c**). As for **4a** with 0.51 (2 mmol) of **10c**. The crude product was sublimed (40°/0.2 Torr): 0.24 g (65%) of **4c**, m.p. 44–45°. UV (hexane): 278 (3.13), 271 (3.23), 266 (3.14), 218 (3.54), 198 (3.78). IR ($CHCl_3$): 2940*m*, 1675*m*, 1600*w*, 1440*m*, 1415*m*, 1320*m*, 1200*w*, 1180*s*, 1050*s*. ^{1}H-NMR ($CDCl_3$): 7.24 (*tm*, ^4J(H,F) = 4, 2H); 2.92 (*m*, 4H); 1.84 (*quint. m*, ^3J(H,H) = 3.5, 4H). ^{13}C-NMR: *Table 3*. ^{19}F-NMR ($CDCl_3$): 82.7 (*ttt* (apparent), ^4J(H,F) = 4, ^6J(H,F) = 1.4). MS: 180 (27, M^+), 165 (11), 159 (6), 151 (7), 129 (9), 115 (11), 101 (5), 75 (8), 63 (10), 51 (14), 47 (100).

*1,1-Difluoro-4,5-dihydro-1*H*,3*H*-cyclopenta[*a*]cyclopropa[*d*]benzene* (**4d**). As for **4a** with **10d** (1.0 g, 4.2 mmol). The crude product was purified by bulb-to-bulb distillation to give **4d** (0.60 g, 86%), m.p. 20–21°. UV (hexane): 277 (3.29), 271 (3.37), 214 (3.61), 199 (3.65). IR ($CHCl_3$): 2960*s*, 2880*m*, 1710 (br.), 1650 (br.), 1530*m*, 1440*m*, 1400*w*, 1360*s*, 1280*s*, 1230*m*, 1210 (br.), 1180*s*, 1150*m*, 1030*m*, 860*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.33 (*tm*, ^4J(H,F) = 4, 2H); 2.99 (*tm*, ^3J(H,H) = 7.5, 4H); 2.12 (*quint.*, ^3J(H,H) = 7.5, 2H). ^{13}C-NMR: *Table 3*. ^{19}F-NMR ($CDCl_3$): 83.6 (*ttt* (apparent), ^4J(H,F) = 3.8, ^6J(H,F) = 2.0). MS: 166 (100, M^+), 151 (21), 146 (16), 115 (46), 99 (7), 75 (10), 63 (15), 51 (12).

*1,1-Difluoro-3,4-dihydro-1*H*-cyclobuta[*a*]cyclopropa[*d*]benzene* (**4e**). As for **4a** with **10e** (0.68 g, 3 mmol). Bulb-to-bulb distillation (50°/0.1 Torr) gave 0.27 g (60%) of **4e** as white, moisture-sensitive crystals, m.p. 30–31°. UV (hexane): 275 (3.45), 269 (3.57), 264 (3.52), 213 (3.74). IR ($CHCl_3$): 2980*w*, 2940*m*, 1680*m*, 1650*s*, 1440*m*,

Table 3. *^{13}C-NMR Data* ($CDCl_3$) *of 1,1-Difluorocyclopropabenzenes*[a])[2])

Cpd.	C(1)	C(1a)/C(5a)	C(2)/C(5)	C(3)/C(4)	Others
4a	101.2 (^1J(C,F) = 303)	128.2 (^2J(C,F) = 21)	115.9 (^3J(C,F) = 1, ^1J(C(2), H) = 170)	145.4 (^4J(C,F) = 3)	20.7 (CH_3)
4b	101.2 (^1J(C,F) = 304)	128.8	117.6 (^3J(C,F) = 2.5)	149.0	140.3 (C(1′)/C(1″) of Ph); 128.0 (C(2′)/C(2″) of Ph); 129.8 (C(3′)/C(3″) of Ph); 127.4 (C(4′)/C(4″) of Ph)
4c	101.0 (^1J(C,F) = 303.8)	127.4 (^2J(C,F) = 20.5)	115.4 (^1J(C(2),H) = 170)	146.3 (^4J(C,F) = 3)	30.5 (CH_2) 22.6 (CH_2)
4d	103.9 (^1J(C,F) = 303.1)	128.3 (^2J(C,F) = 19.7)	111.7 (^1J(C(2),H) = 172)	153.0 (^4J(C,F) = 2.7)	32.5 (CH_2) 25.2 (CH_2)
4e	101.6 (^1J(C,F) = 302.2)	127.0 (^2J(C,F) = 19)	109.6 (^3J(C,F) = 3, ^1J(C(2),H) = 175)	154.2 (^4J(C,F) = 4)	29.9 (CH_2)

[a]) Chemical shifts in ppm relative to TMS (= 0 ppm); coupling constants *J* in Hz. Temp. − 40°.

Table 4. *^{13}C-NMR Data* ($CDCl_3$) *of 1-Fluorocyclopropabenzenyl Cations* **3**[a])[2])

Cpd.	C(1)	C(1a)/C(5a)	C(2)/C(5)	C(3)/C(4)	Others
3a	143.8 (^1J(C,F) = 471)	138.0 (^2J(C,F) = 3)	116.2 (^3J(C,F) = 3, ^1J(C(2),H) = 189)	175.1 (^4J(C,F) = 9)	23.2 (CH_3)
3b	143.8 (^1J(C,F) = 462)	138.1	118.0	173.3 (^4J(C,F) = 8)	137.1 (C(1')/C(1'') of Ph); 129.1 (C(2')/C(2'') of Ph); 130.1 (C(3')/C(3'') of Ph); 131.8 (C(4')/C(4'') of Ph)
3c	142.8 (^1J(C,F) = 473)	136.8 (^2J(C,F) = 3)	115.7 (^1J(C(2),H) = 189)	175.9 (^4J(C,F) = 9)	33.1 (CH_2) 20.2 (CH_2)
3d	145.9 (^1J(C,F) = 472)	138.9	112.3 (^2J(C(2),H) = 191)	183.0 (^4J(C,F) = 8.5)	34.9 (CH_2) 24.8 (CH_2)
3e	145.1 (^1J(C,F) = 475)	138.8 (^2J(C,F) = 2.5)	110.7 (^1J(C(2),H) = 193)	183.2 (^4J(C,F) = 9)	29.4 (CH_2)

[a]) See *Footnote a* of *Table 3*.

1400*w*, 1365*vs*, 1230*vs*, 1150*s*, 1040 (br.), 860*s*, 790*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.14 (*t*, ^4J(H,F) = 3.5, 2H); 3.26 (*t*, ^6J(H,F) = 2.0, 4H). ^{13}C-NMR: *Table 3*. ^{19}F-NMR ($CDCl_3$): 82.1 (*ttt* (apparent), ^4J(H,F) = 3.6, ^6J(H,F) = 1.8). MS: 152 (37, M^+). 151 (100), 149 (9), 140 (14), 133 (16), 125 (9), 102 (23), 99 (8), 85 (10), 75 (22), 71 (19), 69 (59), 63 (20), 17 (65), 51 (28).

1-Fluorocyclopropabenzenyl Cations 3. – To FSO_3D (0.5 ml) in a 5-mm NMR tube cooled to – 78° was added, under Ar, 50 mg of the appropriate difluorocyclopropabenzene **4**. The tube was sealed and stored in liq. N_2. ^{1}H- and ^{13}C-NMR were recorded at – 40° on a *Bruker-WH-360* spectrometer. The ^{19}F-NMR were recorded between – 50 and 20° without temp. control within *ca.* 3 min on a *Varian-XL-200* spectrometer. ^{13}C-NMR of **3**: *Table 4*. *1-Fluoro-3,4-dimethylcyclopropabenzenylium* (**3a**): ^{1}H-NMR: 8.20 (*d*, ^4J(H,F) = 9), 3.08 (*s*, 6H). ^{19}F-NMR: 90.8 (*t*, ^4J(H,F) = 9).

1-Fluoro-3,4-diphenylcyclopropabenzenylium (**3b**): ^{1}H-NMR: 8.35 (br. *d*, ^4J(H,F) = 9, 2H); 7.71 (*m*, 2H); 7.60 (*m*, 4H); 7.50 (*m*, 4H). ^{19}F-NMR: 94.1 (*t*, ^4J(H,F) = 9).

*1-Fluoro-3,4,5,6-tetrahydrocyclohexa[*a*]cyclopropa[*d*]benzenylium* (**3c**): ^{1}H-NMR: 7.95 (*d*, ^4J(H,F) = 8, 2H); 3.37 (br. *s*, 4H); 2.01 (br. *s*, 4H). ^{19}F-NMR: 90.9 (*t*, ^4J(H,F) = 10).

*1-Fluoro-4,5-dihydro-3*H*-cyclopenta[*a*]cyclopropa[*d*]benzenylium* (**3d**): ^{1}H-NMR: 8.20 (*d*, ^4J(H,F) = 8, 2H); 3.70 (*m*, 4H); 2.65 (*m*, 2H). ^{19}F-NMR: 92.2 (*t*, ^4J(H,F) = 9).

*1-Fluoro-3,4-dihydrocyclobuta[*a*]cyclopropa[*d*]benzenylium* (**3e**): ^{1}H-NMR: 8.04 (*d*, ^4J(H,F) = 8, 2H); 4.04 (*s*, 4H). ^{19}F-NMR: 92.1 (*t*, ^4J(H,F) = 8).

REFERENCES

[1] B. Halton, *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349; *Chem. Rev.* **1973**, *73*, 113; W. E. Billups, *Acc. Chem. Res.* **1978**, *11*, 245.

[2] D. Davalian, P. J. Garratt, W. Koller, M. M. Mansuri, *J. Org. Chem.* **1980**, *45*, 4183.

[3] W. E. Billups, B. E. Arney, Jr., L. J. Lin, *J. Org. Chem.* **1984**, *49*, 3437.

[4] U. Burger, P. Müller, L. Zuidema, *Helv. Chim. Acta* **1974**, *57*, 1881; B. Halton, H. M. Hügel, D. P. Kelly, P. Müller, U. Burger, *J. Chem. Soc., Perkin Trans. 2* **1976**, 258.

[5] P. Müller, H. C. Nguyen Thi, *Isr. J. Chem.* **1981**, *21*, 135.

[6] W. v. E. Doering, L. H. Knox, *J. Am. Chem. Soc.* **1957**, *79*, 352.

[7] R. Breslow, J. T. Groves, G. Ryan, *J. Am. Chem. Soc.* **1967**, *89*, 5048.

[8] J. D. Roberts, A. Streitwieser, C. M. Regan, *J. Am. Chem. Soc.* **1952**, *74*, 4579.

[9] B. Halton, D. I. Officer, *Aust. J. Chem.* **1983**, *36*, 1291.

[10] J. M. Photis, L. A. Paquette, *Org. Synth.* **1977**, *57*, 53.

[11] L. A. Paquette, J. D. Kramer, *J. Org. Chem.* **1984**, *49*, 1445; C. Mercier, P. Soncy, W. Rosen, P. Deslongchamps, *Synth. Commun.* **1973**, *3*, 161.

[12] W. J. Baley, H. R. Golden, *J. Am. Chem. Soc.* **1953**, *75*, 4780; A. T. Blomquist, D. T. Longone, *ibid.* **1957**, *79*, 3916.

[13] P. C. Guha, D. K. Sankaran, *Org. Synth., Coll. III* **1955**, 623.
[14] R. N. McDonald, R. R. Reitz, *J. Org. Chem.* **1972**, *37*, 2418.
[15] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, D. T. Longone, *J. Am. Chem. Soc.* **1956**, *78*, 6057; W. J. Baley, W. R. Sorenson, *ibid.* **1954**, *76*, 5421.
[16] A. C. Cope, in 'Organic Reactions', J. Wiley & Sons, Inc., New York, 1975, Vol. 11, pp. 317–493.
[17] J. W. v. Straten, J. J. v. Norden, T. A. M. v. Schaik, G. Th. Franke, W. H. de Wolf, F. Bickelhaupt, Rech. *J. Roy. Neth. Chem. Soc.* **1978**, *97*, 105.
[18] P. D. Bartlett, A. S. Wingrove, R. Owyang, *J. Am. Chem. Soc.* **1968**, *90*, 6067.
[19] V. M. Micovic, M. J. Mihailovic, *J. Org. Chem.* **1953**, *18*, 1190.
[20] A. T. Blomquist, J. A. Verdol, *J. Am. Chem. Soc.* **1955**, *77*, 1806.
[21] D. Rodriguez, Ph. D. Thesis, University of Geneva, 1986.
[22] J. Sepiol, R. C. Soulen, *J. Org. Chem.* **1975**, *40*, 3791.
[23] D. C. F. Law, S. W. Tobey, *J. Am. Chem. Soc.* **1968**, *90*, 2376; K. L. Williamson, Y. F. Littsu, F. H. Hall, S. Swager, M. S. Coulter, *ibid.* **1968**, *90*, 6717; C. W. Jefford, M. Acar, A. Delay, J. Mareda, U. Burger, *Tetrahedron Lett.* **1979**, 1913.
[24] P. Müller, J. Pfyffer, E. Wentrup-Byrne, U. Burger, *Helv. Chim. Acta* **1978**, *61*, 2081.
[25] D. Davalian, P. Garratt, *J. Am. Chem. Soc.* **1975**, *97*, 6883; D. D. Davalian, P. J. Garratt, M. M. Mansuri, *ibid.* **1978**, *100*, 980.
[26] R. P. Thummel, W. Nutakul, *J. Org. Chem.* **1977**, *42*, 300.
[27] H. Günther, G. Zikeli, H. Prestien, *Angew. Chem. Int. Ed.* **1973**, *12*, 762; W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, W. J. Kitching, *J. Org. Chem.* **1976**, *41*, 751.
[28] H. Baumann, H. Olsen, *Helv. Chim. Acta* **1980**, *63*, 2202.
[29] J. C. Perlberger, P. Müller, unpublished results.
[30] B. Halton, M. P. Halton, *Tetrahedron* **1973**, *29*, 1717.
[31] B. Fochlich, G. Welt, *Tetrahedron Lett.* **1978**, 4019.
[32] H. Spiesecke, W. G. Schneider, *Tetrahedron Lett.* **1961**, 468.
[33] R. J. Hunadi, *J. Am. Chem. Soc.* **1983**, *105*, 6889; K. Müllen, *Chem. Rev.* **1984**, *84*, 603; D. G. Farnum, *Adv. Phys. Org. Chem.* **1975**, *11*, 123.
[34] G. A. Olah, P. W. Westerman, D. A. Forsyth, *J. Am. Chem. Soc.* **1975**, *74*, 3419.
[35] D. P. Kelly, G. J. Farquharsou, J. J. Giansiracusa, W. A. Jensen, H. M. Hügel, A. P. Porter, I. J. Rainbow, P. H. Timewell, *J. Am. Chem. Soc.* **1981**, *103*, 3539.
[36] P. Müller, M. Rey, *Helv. Chim. Acta* **1982**, *65*, 1157.