194. Chemistry of Benzocyclopropenes. ^{1}H- and ^{13}C-NMR. Spectra of 2,5-Dideuterio-1-fluorobenzocyclopropenium Ion

by **Paul Müller, Jean Pfyffer, Edeline Wentrup-Byrne** and **Ulrich Burger**

Département de Chimie Organique, Université de Genève, 30, quai Ernest-Ansermet, 1211 Genève, Switzerland

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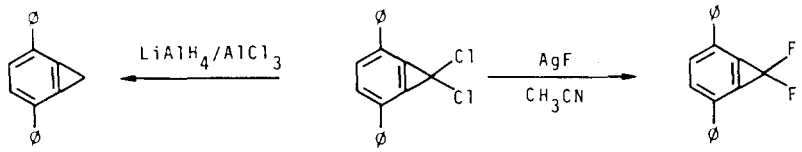
Summary

Preparation of 1,1-difluorobenzocyclopropene (**4**) and of its 2,5- and 3,4-dideuterio derivatives **4a** and **4b** is reported. Upon ionization in cold fluorosulfonic acid, **4** affords 1-fluorobenzocyclopropenium ion (**6**). ^{1}H- and ^{13}C-NMR. spectra of **4** and **6** are assigned on the basis of the data for the specifically deuterium-labelled compounds **4a** and **6a**. Hydrolysis of **6a** leads to 2,5-dideuteriobenzoic acid (**7a**).

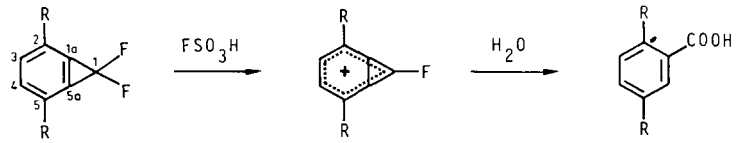
Introduction. – The halogen atoms of 1,1-dihalogenobenzocyclopropenes readily undergo nucleophilic displacements presumably *via* benzocyclopropenium ions. Thus, 1,1-dichloro-2,5-diphenylbenzocyclopropene (**1**) reacts with silver fluoride in acetonitrile at RT. to afford the difluoro compound **2** in almost quantitative yield [1]. With $LiAlH_4/AlCl_3$ the chloro substituents are replaced by hydrogen atoms [2].

Scheme 1



3 **1** **2**

Scheme 2



2 R = Ø
4 R = H

5 R = Ph
6 R = H

7 R = Ø, H

When dihalogenobenzocyclopropenes are dissolved in cold fluorosulfonic acid they ionize to halogenobenzocyclopropenium ions. The stability of these ions at $-50°$ is sufficient for the measurement of their NMR. spectra.

Upon quenching with water they are hydrolyzed to the corresponding benzoic acids **7** [3].

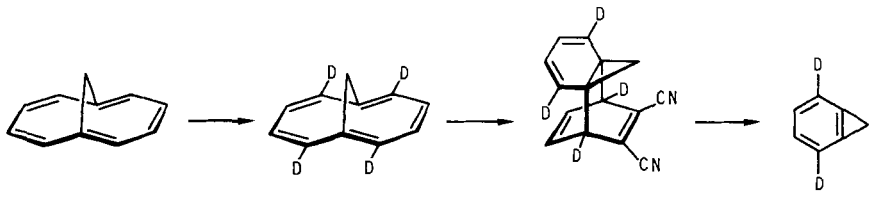
We have reported ^{1}H- and ^{13}C-NMR. spectra [4],[5] of a series of 1,1-dihalogenobenzocyclopropenes and their related benzocyclopropenium ions, most notably of the fluoro derivatives **4** and **6**. For both compounds assignment of the resonance lines to the carbon atoms and protons in positions 2 and 5 as compared to positions 3 and 4 was not unambiguous. It was based on the similarities of analogous resonances in the pairs of compounds, **2** and **4**, and **5** and **6**. This was corroborated by the magnitude of the $J_{H,F}$ and $J_{C,F}$ and by the calculated charge-density [6]. Although all criteria led to an internally consistent argument, experimental verification was desirable. In this communication we report the synthesis and NMR. spectra of 2,5-dideuterio-1,1-difluorobenzocyclopropene (**4a**) and 2,5-dideuterio-1-fluorobenzocyclopropenium ion (**6a**), from which ^{1}H- and ^{13}C-spectra of **4** and **6** can be unambiguously assigned. Furthermore, we describe preparation of various other symmetrically, di- or tetra-deuterated benzocyclopropenes and difluorobenzocyclopropenes which have been prepared in connection with microwave [7] and mass spectroscopic [8] investigations.

Syntheses. – 2,5-Dideuteriobenzocyclopropene (**8a**) has been previously prepared by pyrolysis of the *Diels-Alder* adduct of an appropriately labelled 1,6-methano-[10]annulene (**9**) with dicyanoacetylene [9]:

Although this scheme is in principle also suitable for the preparation of 1,1-difluoro-2,5-dideuteriobenzocyclopropene (**4a**) our approach consists of a modified *Vogel-Tobey* synthesis [10], since the latter method allows one to obtain all the symmetrically dideuterated benzocyclopropenes and difluorobenzocyclopropenes by the same sequence of reactions. In the original *Vogel-Tobey* synthesis the benzocyclopropene skeleton was constructed *via* cycloaddition of butadiene (**10**) to 1,2-dibromo-3,3-difluorocyclopropene (**11**), affording the cycloadduct **12** which upon heating with potassium hydroxide in triethyleneglycol at 80° gave **4** in *ca.* 40% yield.

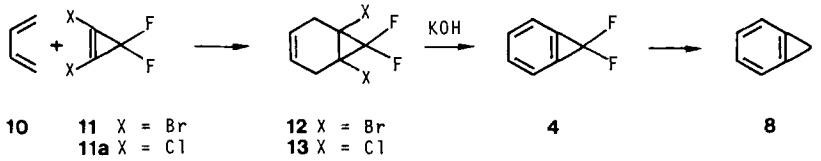
The procedure may be considerably simplified if the more readily available 1,2-dichloro-3,3-difluorocyclopropene (**11a**) [11] is used instead of the 1,2-dibromo compound **11**. Aromatization of the cycloadduct can be effected at low temperature ($\sim -70°$) with potassium *t*-butoxide in dry THF [2]. Deuterium may be introduced by

Scheme 3

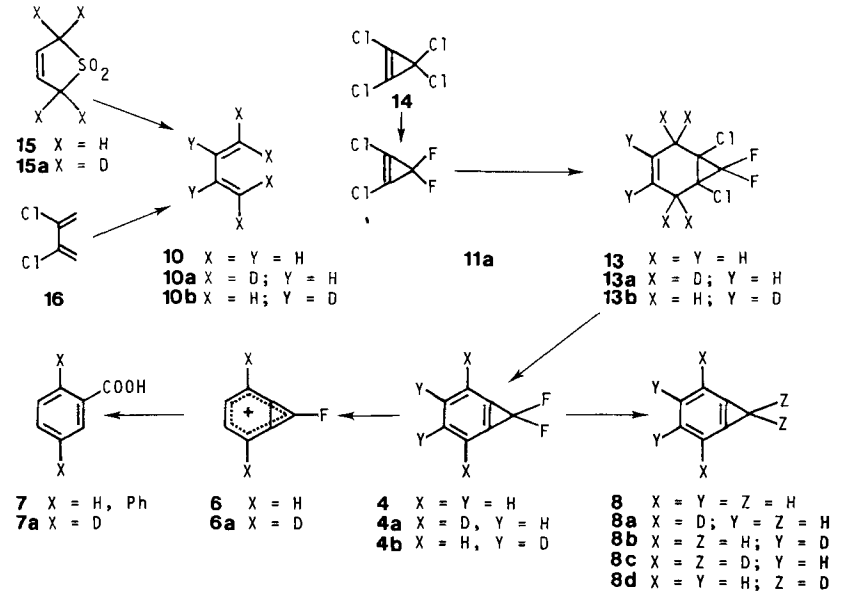


9 **8a**

Scheme 4



Scheme 5



the use of the appropriate 1,1,4,4-tetradeuteriobutadiene (**10a**) or 2,3-dideuteriobutadiene (**10b**) in the cycloaddition step to afford 2,5- and 3,4-dideuterio-1,1-difluorobenzocyclopropene (**4a**) and (**4b**) respectively. Furthermore, the fluoro substituents of **4** to **4b** may be replaced by hydrogen or deuterium to afford the di- and tetradeuteriobenzocyclopropenes **8a**-**8c**. The various reactions are summarized in *Scheme 5*.

1,2-Dichloro-3,3-difluorocyclopropene (**11a**) was obtained by the method of *Tobey & West* [11] on heating tetrachlorocyclopropene (**14**) with a slight excess of antimony trifluoride. The contamination of **11a** with 5–10% of 1,2,3-trichloro-3-fluorocyclopropene can be lowered by using freshly sublimed antimony trifluoride [12]. The deuterated butadienes **10a** and **10b** were prepared by slightly modified literature procedures, 1,1,4,4-tetradeuteriobutadiene (**10a**) by base catalyzed deuterium exchange of 2,5-dihydrothiophene-1,1-dioxide (sulfolene) (**15**) in deuterium oxide [13] followed by pyrolysis [14], and 2,3-dideuteriobutadiene (**10b**) by reduction of the dichloro compound **16** with zinc in dioxane/deuterium oxide, in the presence of sodium iodide and cupric chloride [16]. In contrast to the reaction with unlabelled butadiene, where an excess of diene was present, the cycloaddition of **10a** and **10b** with 1,2-dichloro-3,3-difluorocyclopropene (**11a**) was carried out

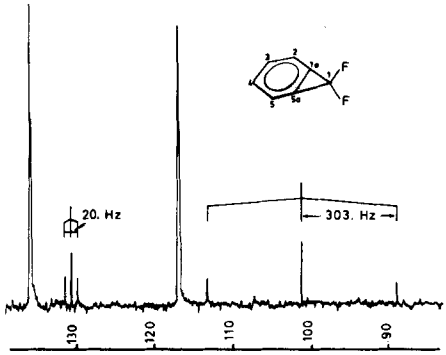


Fig. 1. *^{13}C-FT-NMR. spectrum of 1,1-difluorobenzocyclopropene* (**4**) *in $CDCl_3$ at 25.2 MHz* (^{1}H-noise-decoupled)

with equimolar quantities. The isotopomeric adducts 1,6-dichloro-7,7-difluorobicyclo[4.1.0]hept-3-enes (**13**–**13b**) were treated with freshly sublimed potassium *t*-butoxide in THF at $-70°$ followed by anhydrous work-up [2] to afford the corresponding difluorobenzocyclopropenes **4**–**4b** (40%). The structures of all compounds mentioned were confirmed by NMR. and mass spectral data. The reduction of **4**–**4b** with $LiAlH_4/AlCl_3$ to the corresponding isotopomers of **8** has been previously described [2].

NMR. Spectra. – *Difluorobenzocyclopropene.* The ^{1}H-spectrum of **4** shows the *AA'BB'*-part of a *AA'BB'X*$_2$-system centered at 7.54 ppm. The *B*-protons are coupled with the fluorine atoms ($J_{H,F} = 3.5$ Hz), and were assigned to positions 2 and 5 under the assumption that $^4J_{H,F} > {}^5J_{H,F}$ [10] [18]. In the 2,5-dideuterio compound **4a** H–C(3) and H–C(4) appear as a singlet at 7.65 ppm (CCl_4), while the 3,4-dideuterio isomer **4b** shows a triplet at 7.54 with $^4J_{H,F} = 3.5$ Hz. The preliminary assignments [10] [18] are therefore confirmed on this basis. The ^{13}C-FT-NMR. spectrum of **4** is shown in *Figure 1.*

The triplet at 100.3 ppm ($^1J_{C,F} = 303$ Hz) corresponds to C(1) and the triplet at *129.5 ppm* to C(1a) and C(5a) ($^2J_{C,F} = 20$ Hz). The signals at 116.0 ppm ($^3J_{C,F} = 1$ Hz; $^1J_{C,H} = 175$ Hz) and 134.7 ppm ($^4J_{C,F} = 2.9$ Hz; $^1J_{C,H} = 161$ Hz) can be assigned by comparison with the spectrum of 2,5-dideuterio-1,1-difluorobenzocyclopropene in which the signal at 116 ppm is absent. C(3) and C(4), therefore, resonate at 134.7, and C(2) and C(5) at 116 ppm as suggested [5].

1-Fluorobenzocyclopropenium ions. The ^{1}H-NMR. spectrum of **6** in fluorosulfonic acid consists of the *AA'BB'*-part of an *AA'BB'X*-system with the signals centered at 8.40 and 9.20 ppm (external TMS reference) [4]. With a deuterium label at the C(2) and C(5) positions the spectrum collapses to a singlet at 9.20. The signal at higher field therefore corresponds to the protons at C(2) and C(5). Disappearance of H,F-coupling ($^4J_{H,F} = 9.0$ Hz) upon deuterium substitution at C(2) and C(5) also corroborates the assignments [4]. The ^{13}C-FT-NMR. spectra of **6** and the 2,5-dideuterated ion **6a** are shown in *Figure 2.* Comparison of the spectra demonstrates that C(2) and C(5) resonate at higher field (119.8 ppm) than C(3) and C(4) (158.3).

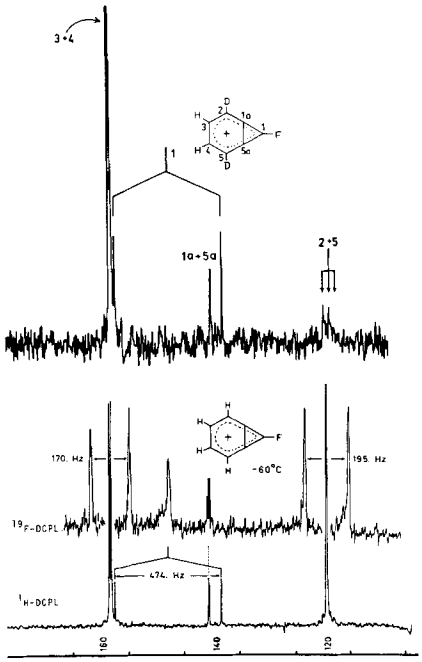


Fig. 2. *^{13}C-FT-NMR. spectra of 1-fluorobenzocyclopropenium cations at 25.2 MHz in FSO_3H* at $-60°$
Bottom: ^{13}C-{^{1}H}-FT-NMR. spectrum of **6**
Center: ^{13}C-{^{19}F}-FT-NMR. spectrum of **6**
Top: ^{13}C-{^{1}H}-FT-NMR. spectrum of **6a**

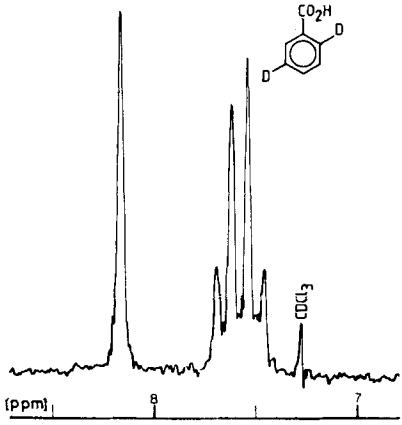
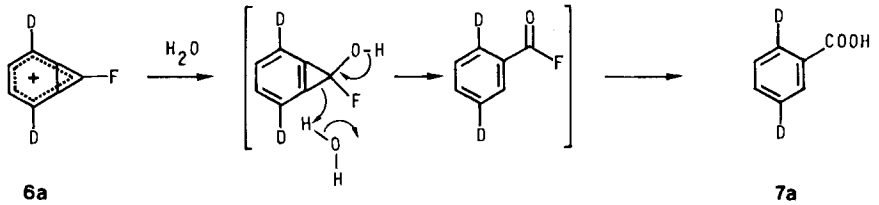


Fig. 3. *^{1}H-NMR. spectrum of 2,5-dideuteriobenzoic acid ($CDCl_3$)*

When solutions of **6a** in fluorosulfonic acid were carefully hydrolyzed, 2,5-dideuteriobenzoic acid (**7a**) was obtained as the only product.

The substitution pattern was deduced from the ^{1}H-NMR. spectrum which shows an *ABM*-spin-system for the aromatic protons *(Fig. 3)*. Neglecting the

Scheme 6



broadening by deuterium, the *M*-proton appears as a singlet at 8.16 ppm. The *A*- and *B*-protons show chemical shifts of 7.65 and 7.50 respectively and couple with 8.5 Hz.

So there is only one proton *ortho* to the carboxylic group (8.16 ppm), the other *ortho* position being occupied by deuterium. The absence of any significant splitting of the line at 8.16 implies that there is no proton in position 5. We may therefore conclude that hydrolysis of **6** involves attack by water at position C(1) exclusively. The 6-membered ring remains intact during the process [19], and only one of the lateral cyclopropane bonds is broken *(Scheme 6)*.

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Experimental Part

General remarks. IR. spectra were recorded in $CHCl_3$ on a *Perkin-Elmer* 257 spectrophotometer and ^1H- and ^{13}C-NMR. spectra on a *Varian* XL-100 instrument in $CDCl_3$. Chemical shifts are expressed in ppm with respect to TMS. Mass spectra were measured on a *Varian* CH-4 spectrometer at 70 eV.

1,2-Dichloro-3,3-difluorocyclopropene (**11a**). Tetrachlorocyclopropene (**14**) (46.7 g, 0.26 mol) and SbF_3 (35 g, 0.2 mol) were heated under reflux for 2 h. After 2 successive destillations **11a** (21.1 g, 56%) was obtained; b.p. 58–60°/720 Torr. VPC. analysis (carbowax column, 75°) revealed 5–10% impurity of 1,2,3-trichloro-3-fluorocyclopropene. Analytical samples of **11a** were purified by preparative VPC. and the compound identified by its ^{19}F-NMR. and MS.

2,2,5,5-Tetradeuterio-2,5-dihydrothiophene-1,1-dioxide (**15a**). A solution of sulfolene (**15**) (100 g), D_2O (100 g) and K_2CO_3 (1 g) was stirred at 50–60° for 2 days. Upon cooling to 4° most of the sulfone cristallized. The product was used for the next exchange step without further treatment. Progress of deuterium exchange was verified by NMR. After 5 successive exchange steps **15a** was dried 24 h at 0.2 Torr (80 g). Analysis of the deuterium content was carried out on the 2,5-dideuterio-1,1-difluorobenzocyclopropene (**4a**) which was composed of 93% D_2- and 7% D_3-isotopomers.

1,1,4,4-Tetradeuterio-1,3-butadiene (**10a**). Pyrolysis of **15a** in batches of 30–40 g between 130° and 170°, following *Charlton & Agagnier* [13] gave **10a** (80–90%).

2,3-Dideuterio-1,3-butadiene (**10b**). The solution of 2,3-dichloro-1,3-butadiene (40 g, 0.33 mol) in 100 ml of dioxane was added over a period of 30 min to a boiling vigourously stirred mixture of 50 ml dry dioxane, Zn dust (45,7 g, 0.7 mol), NaI (1 g), $CuCl_2$ (6 g) and D_2O (14 g, 0.8 mol). Butadiene evolution started immediately. The gas was trapped in 3 successive traps cooled to −70°. The crude product (10 ml) was used without purification for the next step. From the mass spectrum of 3,4-dideuterio-1,1-difluorobenzocyclopropene (**4b**) the isotopic composition of the diene was found to be 97% D_2 and 3% D_3.

2,5-Dichloro-7,7-difluorobicyclo[4.1.0]hept-3ene (**13**) *and deuterated compounds* **13a** *and* **13b**. The cycloaddition of unlabelled butadiene (**10**) and 1,2-dichloro-3,3-difluorobenzocyclopropene (**11a**) was carried out as described by *Tobey et al.* [17]. Compounds **13a** and **13b** respectively were obtained as

follows: tetradeuteriobutadiene (**10a**) (14 g, 0.24 mol) or 2,3-dideuteriobutadiene (**10b**) (6.0 g, 0.11 mol) and **11a** (29.0 g, 0.20 mol) were heated in a steel autoclave at 130° for 22 h. After cooling unreacted diene was allowed to evaporate. Distillation of the remaining solution afforded 20 g (49%) of **13a** (40% of **13b**) boiling at 70°/20 Torr. – MS. of **13**: 202, 200, 198 (M^+, weak), 183, 181, 179 ($M^+ - F$, weak), 165, 163 ($M^+ - Cl$, 80), 127 (100). These fragments are shifted to +4 for **13a** and +2 for **13b**. For ^1H- and ^{19}F-NMR. see [17].

1,1-Difluorobenzocyclopropene **4–4b**. The method of preparation from **13** has been described [2]. ^1H- and ^{13}C-NMR. spectra are discussed in the text. For MS. data see [8].

1-Fluorobenzocyclopropenium ion **6** *and* **6a**. After purification by preparative VPC., **4** and **4a** (100 mg), were injected slowly into 3 ml of freshly distilled fluorosulfonic acid at −70° in a 12 mm NMR. tube under argon. Spectra of the deep orange solution were recorded at −60°.

2,5-Dideuteriobenzoic acid **7a**. The solution of **6a** in fluorosulfonic acid was added carefully to ice water. The solution was extracted with ether. After drying, the organic layer was evaporated and the residue sublimed. The NMR. spectrum of **7a** is shown in *Figure 3*.

Di- and tetradeuteriobenzocyclopropenes **8–8d**. The compounds were prepared by reduction of the appropriate difluorobenzocyclopropenes **4–4b** with $LiAlH_4/AlCl_3$ or $LiAlD_4/AlCl_3$. The reactions were carried out on a 100 mg scale as reported [2]. Pure samples for MS. were obtained by preparative VPC. (SE 30) at 50°.

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