235. Allylic Reactions of Benzocyclopropenes. Discrimination of Halogen Substituents in 1,1-Dihalogenobenzocyclopropenes

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Dedicated to the memory of Professor *Emil Hardegger*

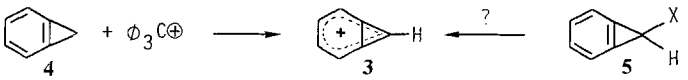
(17.VII.78)

Summary

Reaction of 1,1-dichloro-2,5-diphenylbenzocyclopropene (**10a**) with 1 equiv. of silver fluoride yields 1-chloro-1-fluoro-2,5-diphenylbenzocyclopropene (**10c**). Both **10a** and **10c** react with excess silver fluoride to give the difluoro compound **10b**. Both **10b** and **10c** are also prepared *via* cyclo-additions of 1,2-dichloro-3,3-difluorocyclopropene (**14**) or 1,2,3-trichloro-3-fluorocyclopropene (**13**) with diphenylbutadiene and subsequent aromatization with base. Similarly, 1-chloro-1-fluorobenzocyclopropene (**16**) is accessible from butadiene and **13**.

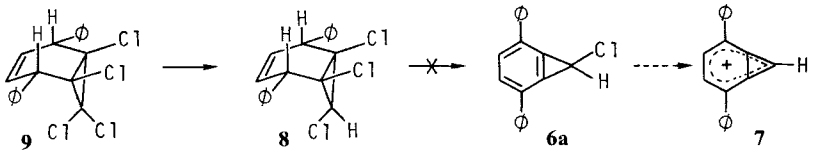
1,1-Dihalogenobenzocyclopropenes **1** are readily accessible precursors for the aromatic yet highly strained 1-halogenobenzocyclopropenium ions [1–4]. Thus the simplest benzocyclopropenium ion **2** known to-date has been obtained by ionization of 1,1-difluorobenzocyclopropene (**1**) in fluorosulfonic acid [3] [4]. Attempts to

generate the parent ion **3** by hydride transfer from benzocyclopropene (**4**) to triphenylmethyl fluoroborate failed [5]. As an alternative approach to **4** we considered ionization of as yet unknown 1-halogenobenzocyclopropenes (**5**). In view of the well-documented instability of dihalogenobenzocyclopropenes **1** [6] [7],



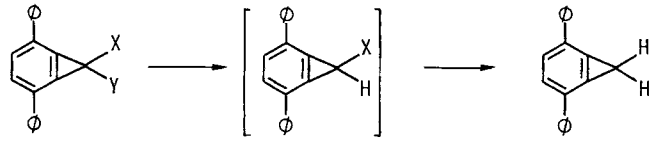
we turned our attention first to the much more stable 2,5-diphenyl derivatives [8] for obtaining a 1-halogeno-2,5-diphenylbenzocyclopropene (**6**) and ultimately 2,5-diphenylbenzocyclopropenium ion (**7**). Our first approach consisted in aromatization of 1,6,7-trichloro-2,5-diphenylbicyclo[4.1.0]hept-3-ene (**8**) available by partial reduction of the *Diels-Alder* adduct **9** of diphenylbutadiene and tetra-

chlorocyclopropene [8]. However, when **8** was treated with 2 equiv. of potassium *t*-butoxide in THF an untractable mixture of products was obtained in which the desired **6a** was not found.



9 **8** **6a** **7**

In a second approach it was attempted to prepare 1-chloro- or 1-fluoro-2,5-diphenylbenzocyclopropene (**6a** or **6b**) by partial reduction of the corresponding 1,1-dihalogeno compounds with $LiAlH_4/AlCl_3$ [9]. Although a variety of conditions were tried, the reaction could not be stopped after displacement of the first halogen substituent. Either the starting compounds **10a** or **10b**, or the hydrocarbon **11** [9] were isolated.



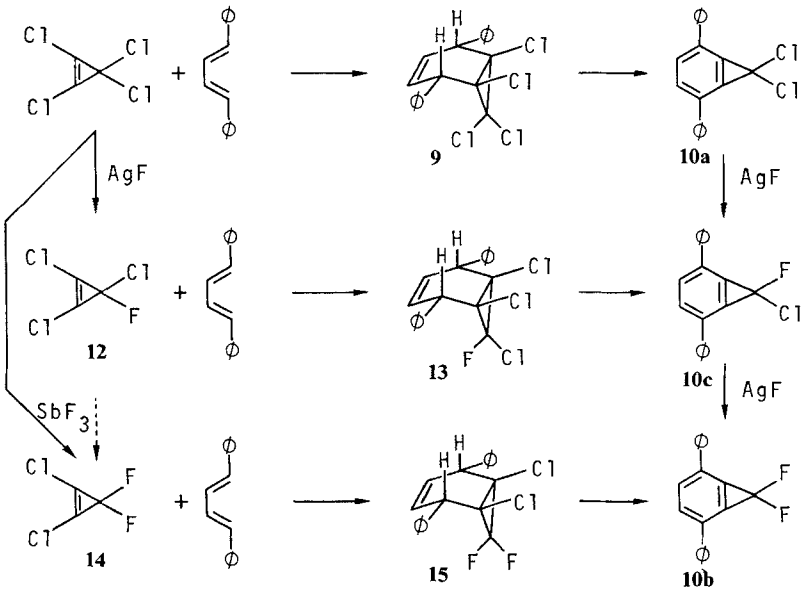
10a X = Y = Cl
10b X = Y = F
10c X = Cl, Y = F

6a X = Cl
6b X = F

11

These observations suggested the use of the 1-chloro-1-fluoro compound **10c** as a more suitable substrate for partial reduction.

Scheme 1



9 **10a** **12** **13** **10c** **14** **15** **10b**

For the synthesis of **10c** we exploit the high reactivity of allylic substituents of 1,1-dihalogenobenzocyclopropenes in reactions leading to benzocyclopropenium ions. Thus treatment of 1,1-dichloro-2,5-diphenylbenzocyclopropene (**10a**) with excess silver fluoride in acetonitrile afforded the difluoro derivative **10b** [10] *(Scheme 1)*. Subsequent work showed that the correct choice of solvent is of crucial importance; when **10a** was stirred with a suspension of silver fluoride in benzene, the difluoro compound **10b** was not formed, but other as yet unidentified products appeared. Furthermore, *Billups* found [11] that benzocyclopropene reacts with silver ion in benzene with opening of the cyclopropane ring, followed by dimerization or addition to added dienes. The chloride-fluoride exchange of **10a** could be stopped at the stage of the chloro-fluoro derivative **10c** by stirring equimolar amounts of organic substrate and silver fluoride in acetonitrile; **10c** could be obtained in *ca.* 40% yield. The structure of the product follows from its spectral data. The ^{1}H-NMR. *(Fig.)* shows the same pattern as that of **10a** and **10b** with the protons of the central ring appearing as a sharp singlet. The position of this signal markedly depends upon the electronegativity of the allylic substituents, *i.e.* the signal of **10a** appears upfield and the signal of **10b** downfield of that of **10c**. Chemical structure proof is provided by conversion of **10c** to the difluoro derivative **10b** with excess silver fluoride as well as by its independent synthesis from diphenylbutadiene and 1,2,3-trichloro-3-fluorocyclopropene (**12**). The latter compound has been obtained previously by *Tobey* as a side-product in the exchange reaction of tetrachlorocyclopropene with SbF_3 [12], which leads mostly to 1,2-dichloro-3,3-difluorocyclopropene (**14**). Halide exchange between tetrachlorocyclopropene and silver fluoride, however, affords **12** in *ca.* 50% yield. When 1,2,3-trichloro-3-fluorocyclopropene (**12**) reacted with diphenylbutadiene under the conditions used for preparation of **9** (120–130°) [8], complete decomposition and polymerization occurred. However, the reaction proceeded smoothly at 80° (2 weeks) in the presence of sodium hydrogen carbonate.

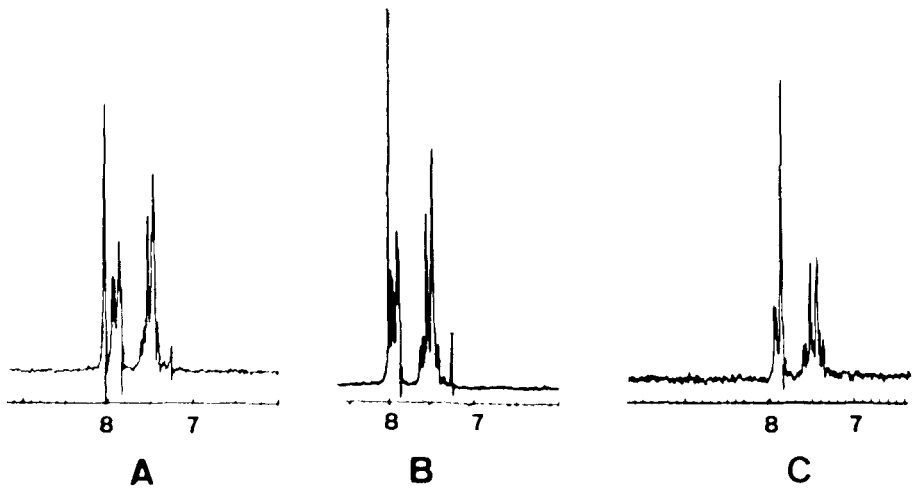


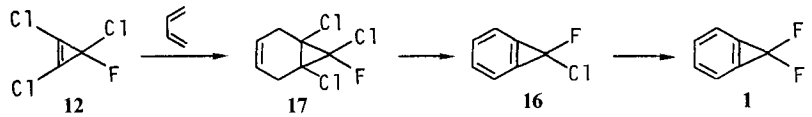
Fig. ^{1}*H-NMR. spectrum of 1,1-dichloro(A), 1-chloro-1-fluoro-(B) and 1,1-difluoro(C)-2,5-diphenylbenzocyclopropenes* **10a–10c**.

The configuration of the cyclo-adduct **13** may be tentatively assigned on the grounds of analogies with other cycloadditions. According to *Tobey* [13], **12** adds *endo* to butadiene and furan in such a way that the chloro substituents are *cis* and fluorine *endo*. The ^{19}F-chemical shift of **13** is 18.6 ppm, similar to the shift of the *endo* fluorine in the adduct of **12** with furan (24.2 ppm) and butadiene (16.6 ppm), which suggests the same configuration in all cyclo-adducts. Treatment of the adduct **13** with 2 equiv. of potassium *t*-butoxide in THF gave 1-chloro-1-fluoro-2,5-diphenylbenzocyclopropene (**10c**) as the only product.

Similarly, reaction of 1,2-dichloro-3,3-difluorocyclopropene (**14**) with diphenylbutadiene at 120° was accompanied by major decomposition and afforded the adduct **15** in 10% yield. Aromatization with base as described for **13** gave 1,1-difluoro-2,5-diphenylbenzocyclopropene (**10b**).

While partial chloride-fluoride exchange appears to be the easiest way to synthesize 1-chloro-1-fluoro-2,5-diphenylbenzocyclopropene (**10c**), the same approach is not suitable for 1-chloro-1-fluorobenzocyclopropene (**16**) itself, owing to the instability of the required precursor, 1,1-dichlorobenzocyclopropene. Fortunately, cyclo-addition of excess butadiene with 1,2,3-trichloro-3-fluorocyclopropene (**12**), although accompanied by partial diene polymerization, proceeds smoothly at 120° to give the adduct **17** *(Scheme 2)*. Aromatization with excess potassium *t*-butoxide in THF at low temperature (−70 to +20°) followed by anhydrous work-up afforded 1-chloro-1-fluorobenzocyclopropene (**16**) in *ca.* 35%

Scheme 2



yield. Although **16** is thermally a very sensitive compound, it could be purified by preparative GC. (Apiezon column, 80°) and stored at −70° for several weeks. The structure of **16** was established by spectroscopic methods. The mass spectrum showed the parent ion (142/144) and peaks corresponding to loss of H, F and Cl (base peak) [16]. A band at 1670 cm^{-1}, characteristic for benzocyclopropenes [6] appeared in the IR. The ^{1}H-NMR. consisted in a unresolved multiplet at $\delta = 7.6$ ppm, which upon F-decoupling collapsed to a symmetrical *AA'BB'*-system. The signal for the fluoro substituent was found as triplet ($J_{H,F} = 2.0$ Hz) at 97.5 ppm downfield from C_6F_6, in good agreement with the chemical shift observed for **10c**. By analogy with 1,1-difluorobenzocyclopropene (**1**) the H,F-coupling is assigned to the protons in positions 2 and 5 [4]. The ^{13}C-NMR. spectrum of **16** is very similar to that of **1** [4]. The signal at 115.7 ppm is assigned to C(2) and C(5), while the singlet at lower field (134.4 ppm) corresponds to C(3) and C(4). This assignment follows from the spectrum of **1** where C(2) and C(5) resonate at higher field than C(3) and C(4) [4]. The doublet with the larger C,F-coupling ($J_{C,F} = 318$ Hz) at 84.6 ppm is assigned to C(1) while the doublet with $J_{C,F} = 20.5$ Hz at 132.1 ppm must correspond to C(1a) and C(5a).

1-Chloro-1-fluorobenzocyclopropene (**16**) could be converted to the difluoro derivative **1** by reaction with silver fluoride in acetonitrile as described for **10c**. However, partial reduction to the 1-fluorobenzocyclopropenes **5** or **6b** has so far met with only limited success. Treatment of the diphenyl derivative **10c** with zinc borohydride afforded a thermally very unstable product, which started to decompose in the NMR. probe. In order to prevent total decomposition, it was further reduced to give 2,5-diphenylbenzocyclopropene (**11**). Experiments toward isolation and full characterization of this supposed 1-fluoro-2,5-diphenylbenzocyclopropene (**6b**) are now under way.

Financial support of this work by the *Fonds National Suisse de la Recherche Scientifique* (projects No. 2.522-0.76 and 2.1280.74) is gratefully acknowledged. The authors thank Mr. *J.-P. Saulnier* for the NMR. measurements and Dr. *U. Burger* for help in the interpretation.

Experimental Part

General remarks. IR. spectra were recorded in $CHCl_3$ on a *Perkin-Elmer* 257 spectrophotometer and ^{1}H- and ^{13}C-NMR. spectra on a *Varian* XL-100 instrument in $CDCl_3$. Chemical shifts are expressed in ppm with respect to tetramethylsilane taken as zero. ^{19}F-Chemical shifts are measured downfield from C_6F_6. Mass spectra were measured on a *Varian* CH-4 spectrometer at 70 eV.

1,1-Difluoro-2,5-diphenylbenzocyclopropene (**10b**) *from* **10a** *by halide exchange.* 1,1-Dichloro-2,5-diphenylbenzocyclopropene (**10a**) [8] (220 mg, 0.7 mmol) was stirred with AgF (1.0 g, 7.9 mmol) suspended in 50 ml of acetonitrile for 24 h in the dark. After filtration, the solution was evaporated and the solid residue was purified by chromatography in benzene on silica gel. Recrystallization with benzene/pentane gave 167 mg (85%) 1,1-difluoro-2,5-diphenylbenzocyclopropene (**10b**), m.p. 161–163°. UV.: (cyclohexane): λ_{max} 315 nm (logε 4.63). – IR. ($CHCl_3$): $\tilde{\nu}$(C=C) 1675 cm^{-1}. – ^{1}H- and ^{13}C-NMR. spectra are reported in the *Figure* and ref. [2] [9]. – ^{19}F-NMR. ($CDCl_3$): 79.9 (*s*). – MS.: 278 (M^+, 100), 277 ($M^+ - H$, 37), 259 ($M^+ - F$, 13), 257 (27), 226 (10), 201 ($M^+ - C_6F_6$, 12).

1-Chloro-1-fluoro-2,5-diphenylbenzocyclopropene (**10c**) *by halide exchange.* 1,1-Dichloro-2,5-diphenylbenzocyclopropene (**10a**) (1.0 g, 3.2 mmol) and AgF (410 mg, 3.2 mmol) were stirred in 30 ml of dry acetonitrile. Precipitation of AgCl started almost immediately. After 2 h, the solution was filtered, concentrated and the product was recrystallized from acetonitrile. Yield 350 mg (37%) of **10c**, m.p. 145–146°. – IR.: $\tilde{\nu}$(C=C) 1695 cm^{-1}. – ^{1}H-NMR.: *Figure*. – ^{19}F-NMR.: 97.8 (*s*). – MS.: 296, 294 (M^+, 40), 275 ($M^+ - F$, weak), 259 ($M^+ - Cl$, 100), 258 ($M^+ - HCl$, 54), 257 ($M^+ - H_2Cl$, 70), 239 ($M^+ - HClF$, 30).

A mixture of 26 mg of **10c** and 50 mg of AgF in 10 ml of acetonitrile was stirred for 12 h. After filtration, the solvent was evaporated. The ^{1}H-NMR. spectrum of the residue was identical to that of independently prepared **10b**.

1,6-Dichloro-7,7-difluoro-2,5-diphenylbicyclo[4.1.0]hept-3-ene (**15**). A solution containing 1,2-dichloro-3,3-difluorocyclopropene [12] (**14**) (6.5 g, 45 mmol) and 1,4-diphenyl-1,3-butadiene (5.6 g, 27 mmol) in 60 ml of CCl_4 was heated in a steel autoclave to 130° for 60 h. After evaporation of the solvent, unreacted diphenylbutadiene was removed by sublimation (120°/12 Torr). The tarry residue was transferred to a 'bulb-tube'. At 130°/12 Torr, 1.05 g of **15** (11%) sublimed, m.p. 124–125° (from pentane). – ^{1}H-NMR.: 7.33 (*s*, 10 H); 5.76 (*d*, 2 H); 4.20 (*m*, 2 H). – ^{19}F-NMR.: 18.4 (*d*, $J_{F,F}$ = 150 Hz); 32.8 (*d*, $J_{F,F}$ = 150 Hz). – MS.: 354 (weak), 352 (weak), 350 (M^+, *s*), 317, 315 ($M^+ - Cl$, 55), 279 ($M^+ - HCl_2$, 23), 259 (35), 225 (45), 180 (100).

1,1-Difluoro-2,5-diphenylbenzocyclopropene (**10b**) *from* **15**. To potassium *t*-butoxide (400 mg, 3.6 mmol) in 50 ml of dry THF at – 60° was added dropwise 1,6-dichloro-7,7-difluoro-2,5-diphenylbicyclo[4.1.0]hept-3-ene (**15**) (500 mg, 1.4 mmol) in 30 ml of THF. The solution was stirred at – 30° for 1 h before it was allowed to warm to RT. After evaporation of the solvent, the residue was extracted with ether, the extract concentrated and recrystallized from cyclohexane. Yield 30 mg (77%) of **10b**, identified by comparing the spectral data with those of a sample obtained by halide exchange.

1,2,3-Trichloro-3-fluorocyclopropene (**12**). To 13 g of AgF cooled to – 50° was added dropwise with vigorous stirring tetrachlorocyclopropene [15] (19 g, 0.11 mol) over a period of 5 min. The flask was

then slowly heated to 120°. After 2.5 h a second portion of AgF (10 g, total amount 0.18 mol) was added at once to the cooled mixture, and heating was continued for a further 6 h. Distillation afforded a liquid containing **12** together with tetrachlorocyclopropene and **14**. Distillation *(Vigreux)* gave 1,2,3-trichloro-3-fluorocyclopropene (6.8 g, 40%). Analytical samples were by preparative GC. The physical and spectral data are reported elsewhere [15].

1,6,7-Trichloro-7-fluoro-2,5-diphenylbicyclo[4.1.0]hept-3-ene (**13**). 1,2,3-Trichloro-3-fluorocyclopropene (**12**) (0.58 g, 3.6 mmol) and 1,4-diphenylbutadiene (0.66 g, 3.2 mmol) in 20 ml of CCl_4 containing 0.25 g of $NaHCO_3$ were heated in a sealed tube to 80° during 15 days. The crude reaction mixture was purified by column chromatography in CCl_4 on silica gel and gave 680 mg of **13** (58%), m.p. 138–42° after recrystallization from hexane. – ^{1}H-NMR.: 7.35 (*s*, 10 H); 5.75 (*d*, 2 H); 4.20 (*d*, 2 H). – ^{19}F-NMR.: 18.6 (*s*).

1-Chloro-1-fluoro-2,5-diphenylbenzocyclopropene (**10c**) *from* **13**. A solution of **13** (100 mg, 0.27 mmol) in 20 ml of THF was added to a suspension of 73 mg (0.65 mmol) of potassium-*t*-butoxide in 20 ml of THF at −50°. After addition the solution was allowed to warm to RT. and stirring was continued for 6 h. Work-up as described for **10b** afforded 48 mg (60%) of **10c**.

1,6,7-Trichloro-7-fluorobicyclo[4.1.0]hept-3-ene (**17**). Butadiene (30 g, 0.6 mol) and 1,2,3-trichloro-3-fluorocyclopropene (**12**) (7.0 g, 40 mmol) were heated with 40 ml of CCl_4 in a steel autoclave containing 30 mg of K_2CO_3 (to suppress polymerization) at 100° for 24 h. After cooling, the autoclave was opened and the solution was warmed to RT. in order to allow evaporation of unreacted butadiene. Distillation gave 5.85 g of **17** (65%), b.p. 90°/12 Torr, identified by comparison of the spectral data with those reported by *Tobey* [13].

1-Chloro-1-fluorobenzocyclopropene (**16**). To potassium *t*-butoxide (2.0 g, 18 mmol) suspended in 150 ml of THF at −70° was added 1,6,7-trichloro-7-fluorobicyclo[4.1.0]hept-3-ene (**17**) (3.0 g, 14 mmol) dissolved in 10 ml of THF under N_2. After 4 h stirring the solution was allowed to warm to RT. A second portion of potassium *t*-butoxide (2.0 g, 18 mmol) was added and stirring was continued for 2 additional h. After cooling to −70° the mixture was centrifuged, filtered, and the precipitate extracted with 25 ml of pentane. The solvents were evaporated at 20–40°/12 Torr. Crude yield 1.1 g containing 0.74 g (37%) of **16**. The product was purified by preparative GC. (60 cm Apiezon column at 80°). The spectral data are discussed in the theoretical part.

1,1-Difluorobenzocyclopropene (**1**) *from* **16**. To AgF (200 mg) suspended in 4 ml of CD_3CN at −40° was added 1-chloro-1-fluorobenzocyclopropene (**16**) (50 mg) with vigorous stirring. After 25 min the solution was warmed to 0° and allowed to stand at this temperature for 20 min. After filtration, the solution was analyzed by GC. (80°, Apiezon column). The starting compound **16** had completely disappeared and difluorobenzocyclopropene (**1**) was present in *ca.* 60% yield (by integration). **1** was identified by the retention time and ^{19}F-NMR.

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