

## 202. 1-Fluoro-benzocyclopropenium Ion from 1,1-difluoro-benzocyclopropene

by Ulrich Burger, Paul Müller and Laura Zuidema<sup>1)</sup>

Département de Chimie Organique, Université de Genève, 1211 Genève 4.

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*Summary.* 1,1-Difluoro-benzocyclopropene (**1**) ionizes in fluorosulphonic acid to yield the cation **2**, which is stable at  $-50^\circ$  for several hours. Upon quenching with water **2** affords benzoic acid.

Benzocyclopropenium ions have been postulated to exist as reactive intermediates in allylic reactions of several benzocyclopropenes [1–3]. Recently the 1-chloro-2,5-diphenyl-benzocyclopropenium ion has been prepared from 1,1-dichloro-2,5-diphe-

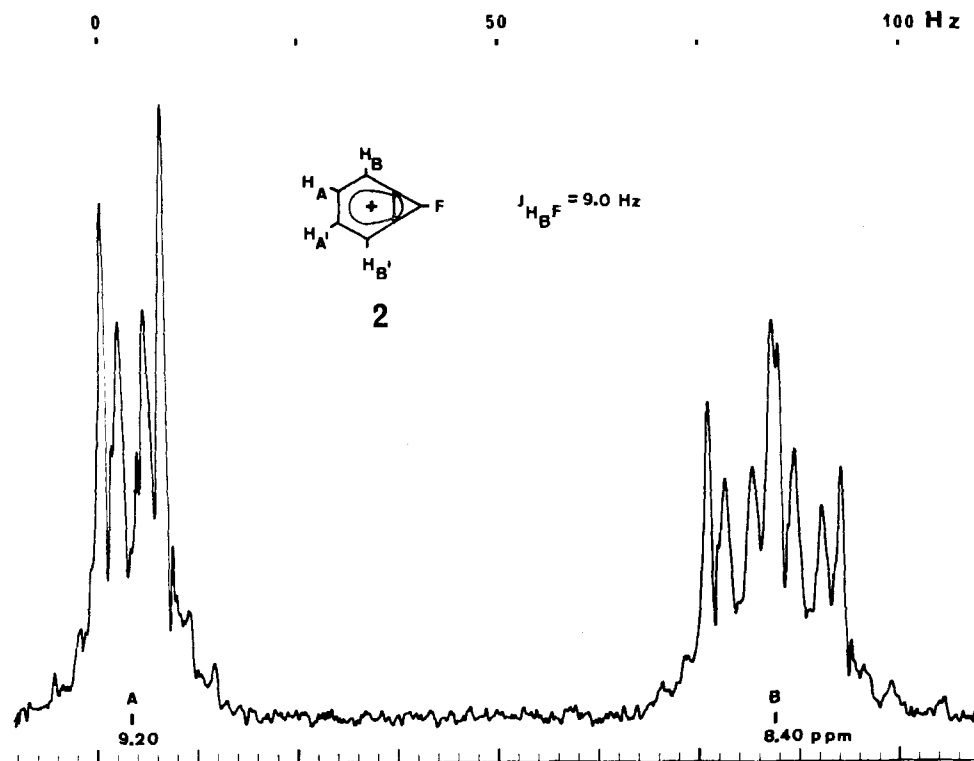


Fig. 1. <sup>1</sup>H-NMR. spectrum of 1-fluoro-benzocyclopropenium ion (**2**) in FSO<sub>3</sub>H at  $-50^\circ$  (standard TMS. external)

<sup>1)</sup> On leave from Hope College, Holland, Michigan.

nyl-benzocyclopropene, and its NMR. spectrum has been reported [4]. By using the same procedure<sup>2)</sup> we have obtained the 1-fluoro-benzocyclopropenium ion (2).

1,1-Difluoro-benzocyclopropene (1) was dissolved at  $-70^\circ$  in freshly distilled fluorosulphonic acid under nitrogen. The solution was stable at  $-50^\circ$  for several hours. The  $^1\text{H-NMR}$ . spectrum, observed at 100 MHz showed two multiplets of equal intensities centered at 8.40 (*B*-protons) and 9.20 ppm (*A*-protons) downfield from external TMS. (Fig. 1). The splitting pattern corresponds to an  $AA'BB'X$  system, where X represents the fluorine. Decoupling of the *B*-protons results in a singlet at 9.20 ppm (Fig. 2) while decoupling of the *A*-protons gives a doublet at

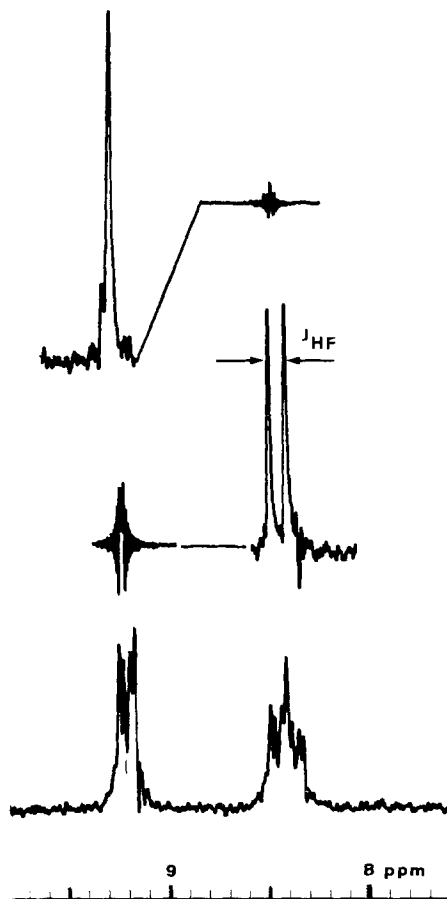


Fig. 2. Decoupling experiments with 1-fluoro-benzocyclopropenium ion (2)

8.40 ppm with  $J_{\text{HF}} = 9.0$  Hz. The *B*-protons are assigned to the positions 2 and 5 in analogy to the assignment in the parent 1,1-difluoro-benzocyclopropene [5], where  $^4J_{\text{HF}}$  only is important. The appearance of the *A*-protons at lower field (9.20 ppm)

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is in agreement with the calculated higher positive charge densities at positions 3 and 4 in comparison with 2 and 5 [6].

In the  $^{19}\text{F}$ -NMR. spectrum of **2** the fluorine appears as triplet ( $J_{\text{HF}} = 9.0$  Hz) at 101 ppm downfield from external  $\text{C}_6\text{F}_6$ . The fluorine signal is shifted 20 ppm downfield with respect to that of **1**. The deshielding of the protons in comparison with **1** is 0.8 and 1.6 ppm, in good agreement with the 1.5 ppm observed in the 1,1-dichloro-2,5-diphenyl-benzocyclopropene case [4].

Quenching of **2** with water affords benzoic acid as the only product. This result is best explained by attack of water at position 1 of **2**, followed by ring opening and subsequent hydrolysis of the intermediate benzoyl fluoride.

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## REFERENCES

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### 203. Silberioneninduzierte Reaktion von 3-Chlor-2-pyrrolidino-cyclohexen mit 1,3-Dienen

Vorläufige Mitteilung<sup>1)</sup>

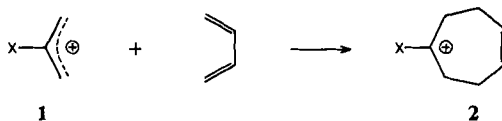
von Rudolf Schmid<sup>2)</sup> und Hans Schmid

Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

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*Summary.* 3-Chloro-2-pyrrolidinocyclohexene (**3**) in the presence of silver tetrafluoroborate in methylene chloride at  $-60^\circ$  underwent cycloadditions with various 1,3-dienes; the resulting iminium tetrafluoroborate salts **4a–8a** were hydrolysed to give the bicyclic and tricyclic ketones **4b–8b**. The addition reactions can be regarded as [3+4]-cycloadditions of an intermediate 2-aminoallyl cation.

Cycloadditionen von Allylkationen des Typus **1** an 1,3-Diene stellen eine wertvolle, vielfältig anwendbare Methode zum Aufbau von siebengliedrigen Carbocyclen (**2**) dar [1].



<sup>1)</sup> Eine ausführliche Mitteilung soll in dieser Zeitschrift erscheinen.

<sup>2)</sup> Teil der geplanten Dissertation, Universität Zürich.