Isolation and Ionization of 1,1-Dihalogeno-1*H*-cyclopropa[*a*]-naphthalene**

Paul Müller* and Huong Can Nguyen Thi

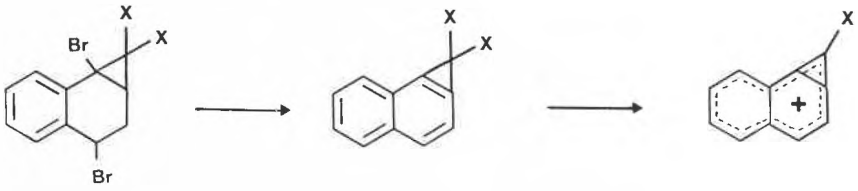
Abstract: 1,1-Difluoro- and 1,1-dichloro-1*H*-cyclopropa[*a*]naphthalenes (**1a** and **1b**) are prepared via dehydrohalogenation of the appropriate brominated carbene adducts (**2a** and **2b**, respectively) of 4-bromo-1,2-dihydronaphthalene. Upon dissolution of **1a** in cold fluorosulfonic acid it furnishes the very short-lived cation **3**; the latter is characterized by its ^{1}H- and ^{19}F-NMR spectra.

Although all cycloproparenes are highly strained, their kinetic stability varies considerably with their structure. Thus, the linearly benzanellated 1*H*-cyclopropa[*b*]-naphthalene[1] and 1*H*-cyclopropa[*b*]-anthracene[2] as well as their 1,1-dihalogeno derivatives[3,4] show only moderate reactivity, and they may be isolated and stored at ambient temperatures. In contrast, the isomeric 1*H*-cyclopropa[*a*]-naphthalene decomposes at + 20 °C[5] upon melting and 1*H*-cyclopropa[*l*]-phenanthrene at − 78 °C over a period of days[6]. Similarly, 1,1-difluoro-1*H*-cyclopropa[*a*]naphthalene (**1a**) has only been observed under NMR conditions at − 30 °C[7] while attempts to isolate 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene failed[8]. We now report a modified experimental procedure which enables preparation of pure solutions of **1a** and its 1,1-dichloro derivative **1b**.

The difluoro compound **1a** is obtained upon slow addition of potassium *tert*-butoxide (2.2 mmol) in tetrahydrofuran (THF) (3.8 mL) to the precursor **2a**[7] (0.75 mmol) in dry THF at − 78 °C under N_2. The solution is warmed up to − 35 °C and the solvent is evaporated at 0.7 Torr (2.5 h). The residue is treated with pre-cooled hexane (3 mL) and the solution is filtered at low temperature into a two-neck flask connected via a filtering disk to a 5 mm NMR tube. The filtrate is evaporated to dryness as above. The residue is dissolved in cold CD_2Cl_2 (0.6 mL) and filtered into the NMR tube.

The ^{1}H-NMR spectrum of **1a** (Fig. 1) recorded at 360 MHz shows a similar pattern as reported previously at 100 MHz in [$^2H_8$]THF/[$^2H_8$]toluene, however the signals are shifted downfield by ca. 0.7 ppm. The lines attributed to H-C(2) (δ = 7.54, J(HF) = 4 Hz) and H-C(3) (δ = 8.15) are clearly distinguishable from the multiplets for the protons at C(5), C(6) centered at δ = 7.70 and C(4), C(7) centered at δ = 8.05. The vicinal coupling constant (J_{AB}) for H-C(2) and H-C(3) is 7.5 Hz, in good agreement with the value reported for vicinal coupling in 1*H*-cyclopropa[*a*]-naphthalene[5].

The same procedure applied to **2b** afforded 1,1-dichloro-1*H*-cyclopropa[*a*]-naphthalene **1b**, which has a vicinal coupling constant of 7.5 Hz. In the ^{1}H-NMR spectrum of **1b** the signal of H-C(3) is superimposed over the multiplets attributed to H-C(4), H-C(7) at δ = 8.05. While **1b** decomposed rapidly in solution, a ^{13}C-NMR spectrum could be obtained with the difluoro compound **1a**. Tentative assignment of the lines was made on the grounds of correlations with other cycloprop-



2a: X = F
2b: X = Cl

1a: X = F
1b: X = Cl

3: X = F

arenes: δ = 101.7 (C(1), t, J(C,F) = 300 Hz), 128.2 (t, J(C,F) = 20 Hz) and 129.4 (t, J(C,F) = 19 Hz) (C(1a) and C(7b)), 112.4 (C(2)), 125.3 (C(3)), 136.9 (C(3a)), 137.4 (C(7)), 120.6 (C(7a)), 129.0, 129.9,

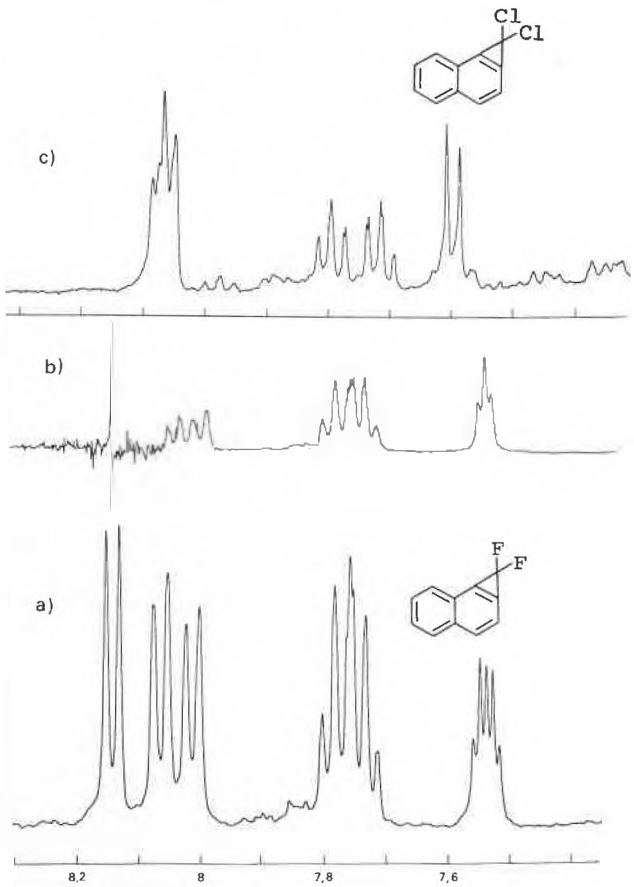


Fig. 1. ^{1}H-NMR spectra of 1,1-dihalogeno-1H-cyclopropa[a]naphthalenes: a) **1a**; *b)* **1a**, *decoupled at H-C(3); c)* **1b**.

* *Correspondence:* Prof. Dr. P. Müller
Département de Chimie Organique
Université de Genève
30, quai Ernest-Ansermet, CH-1211 Genève 4

** This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (grant No. 2.034-0.83). We are indebted to Prof. E. Vogel (Universität Köln) and Prof. B. Halton (Victoria University of Wellington) for communication of results prior to publication.

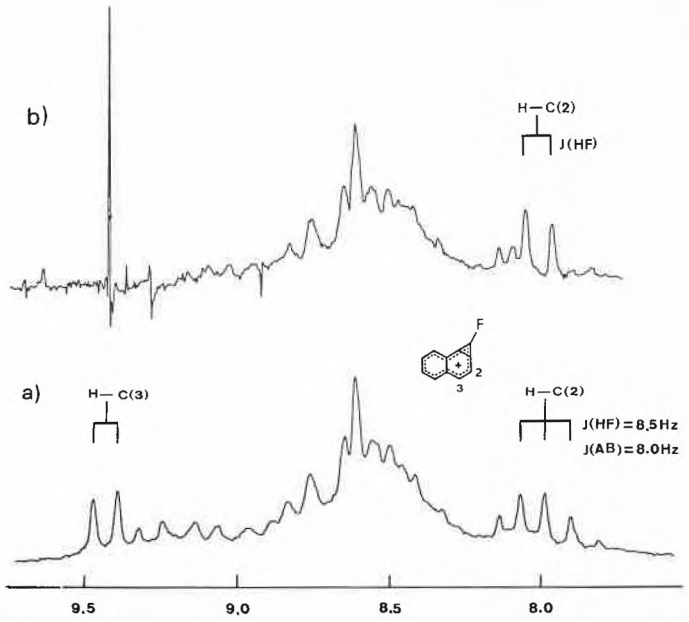


Fig. 2. ^{1}H-NMR spectra of 1-fluoro-1H-cyclopropa[a]naphthalenium ion **3**: *a) undecoupled; b) decoupled at H-C(3).*

130.7 (C(4), C(5), C(6)). As is the case with other cycloproparenes, the tertiary carbon atom adjacent to the cyclopropene ring (C(2)) resonates at ca. 10–15 ppm higher field than all others. By analogy the highest lying quaternary resonance line is assigned to C(7a).

Attempts to ionize **1a** to the cation **3** met only with limited success. When a cooled CD_2Cl_2 solution containing **1a** was added to fluorosulfonic acid at −78 °C, a dark orange solution was obtained. ^{1}H- and ^{19}F-NMR spectra of this solution are consistent with the structure of the fluoro cation **3**. The ^{19}F-NMR spectrum (recorded at −50 °C, 100 MHz) shows a doublet at $\delta = 89$ downfield from C_6F_6 with $J(H,F) = 8.5$ Hz. Other fluorocycloproparenium ions have F-resonances at $\delta = 101$ [9] and 108 [3] and H, F couplings of 9 and 10 Hz, respectively. In the ^{1}H-NMR spectrum of **3** the signals are shifted downfield into the range of $\delta = 7.9$ to 9.5 (Fig. 2). Partial decomposition of the sample precludes detailed analysis of the spectrum. However, the lines of H-C(2) ($\delta = 7.98$, t) and H-C(3) ($\delta = 9.43$, d) can be assigned on the grounds of decoupling experiments. Thus the signal at $\delta = 7.98$ collapses to a doublet upon F-decoupling with $J(AB) = 8$ Hz, and a doublet with $J(H,F) = 8.5$ Hz is obtained upon irradiation of the signal of H-C(3) at $\delta = 9.43$. Additional evidence for the intermediacy of 1-fluoro-1*H*-cyclopropa[*a*]naphthalenium ion **3** is provided by the previously [7] reported reaction of **1a** with methanol, which leads to a mixture of methyl 1- and 2-naphthoate. Similarly, acid catalyzed methanolysis of **1b** afforded methyl 1-naphthoate (10%) and the 2-isomer (44%).

Received: October 11, 1985 [FC39]

[1] W.E. Billups, W.Y. Chow, *J. Am. Chem. Soc. 95* (1973) 4099.
[2] W.E. Billups, E.W. Casserly, B.E. Arney Jr., *J. Am. Chem. Soc. 106* (1984) 440.
[3] P. Müller, H.C. Nguyen Thi, *Isr. J. Chem. 21* (1981) 135.
[4] P. Müller, M. Rey, *Helv. Chim. Acta 64* (1981) 354; *65* (1982) 1157; P. Müller, D. Rodriguez, *ibid. 66* (1983) 2540.
[5] S. Tanimoto, R. Schäfer, J. Ippen, E. Vogel, *Angew. Chem. 88* (1976) 643; *Angew. Chem. Int. Ed. Engl. 15* (1976) 613.
[6] B. Halton, B.R. Dent, S. Böhm, D.L. Officer, H. Schmickler, F. Schophoff, E. Vogel, *J. Am. Chem. Soc.*, in print.
[7] P. Müller, H.C. Nguyen Thi, *Helv. Chim. Acta 67* (1984) 467.
[8] B.R. Dent, B. Halton, *Tetrahedron Lett. 25* (1984) 4279.
[9] U. Burger, P. Müller, L. Zuidema, *Helv. Chim. Acta 57* (1974) 1881.