57. 1,1-Difluoro-1*H*-cyclopropa[*a*]naphthalene

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(12.I.84)

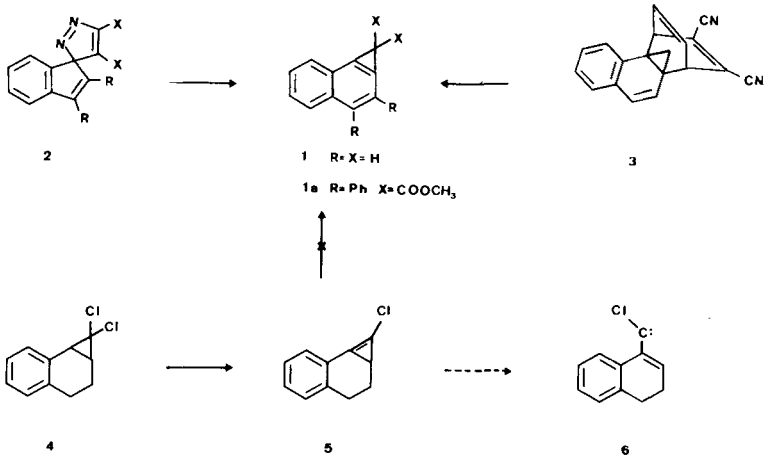
Summary

1,1-Difluorocyclopropa[*a*]naphthalene (**1b**) is prepared in three steps from 4-bromo-1,2-dihydronaphthalene (**7**) *via* carbene addition, benzylic bromination and bis-dehydrohalogenation. Structural evidence for formation of **1b** is based on ^{1}H- and ^{19}F-NMR spectroscopy. Compound **1b** is stable in solution at −30°. Upon reaction with MeOH/H$^+$ it is converted to a 1:2 mixture of 1- and 2-methylnaphthoate (**10** and **11**, respectively).

The synthesis of 1*H*-cyclopropa[*a*]naphthalenes has been achieved by two approaches. The derivative **1a** was obtained by photolysis of the substituted spiro-3*H*-pyrazole **2** [1], while the parent compound **1** was prepared by pyrolysis of the *Diels-Alder* adduct **3** of 2,3-benzo-1,6-methano[10]annulene and dicyanoacetylene [2] *(Scheme 1)*.

A very simple synthesis of **1** would consist in the dehydrohalogenation of the dichlorocarbene adduct **4** of 1,2-dihydronaphthalene under the condition of the *Billups* procedure for preparation of benzocyclopropene and 1*H*-cyclopropa[*b*]naphthalene [3].

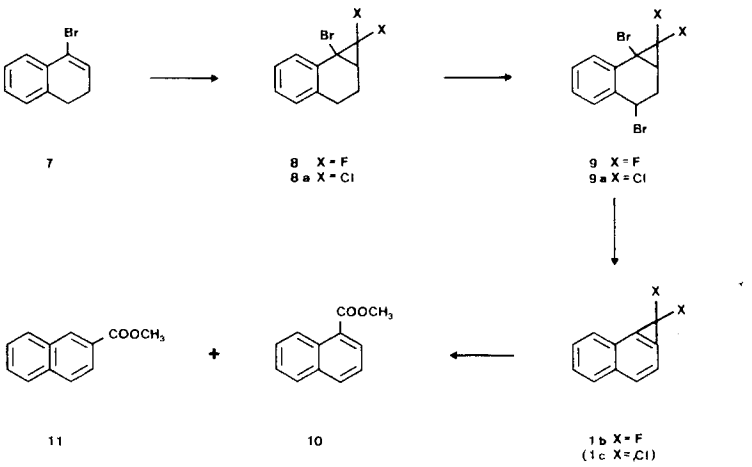
Scheme 1



This approach has been tried by several groups, but only ring-opened naphthalene derivatives were isolated [4]. The failure of the approach may be rationalized by formation of an intermediate chlorocyclopropene **5** which undergoes ring opening to yield the chlorocarbene **6** instead of further aromatization to **1.** The intermediacy of cyclopropenes analogous to **5** has been demonstrated in related dehydrohalogenation reactions of chlorocyclopropanes [5].

We speculated that a dehydrohalogenation route towards **1** would be successful if formation of cyclopropenes **5,** where the double bond is located exocyclic to the cyclohexane ring, could be suppressed. Accordingly, we developed the short synthesis outlined in *Scheme 2* which allows preparation of 1,1-difluoro-1*H*-cyclopropa[*a*]-naphthalene (**1b**). The latter could be observed under NMR conditions.

Scheme 2



The starting compound, 4-bromo-1,2-dihydronaphthalene (**7**), readily available from 1,2-dihydronaphthalene *via* bromine addition followed by dehydrobromination [6], undergoes addition of difluorocarbene [7] or dichlorocarbene [8] to yield **8** and **8a** in 27 and 85% yields, respectively. The benzylic bromo substituent was introduced by reaction with *N*-bromosuccinimide (NBS). The spectra of the bromo derivatives **9** and **9a** are consistent with the proposed structure, however, the configuration of the compounds could not be established owing to identical *cis*- and *trans*-coupling constants of H–C(2) with H–C(3). Although a variety of conditions were tried to effect bis-dehydrohalogenation of the dichloro derivative **9a,** no characterizable products could be isolated from the reaction. However, treatment of the difluoro compound **9** with excess *t*-BuOK at −78°, followed by anhydrous workup at low temperature allowed observation of the ^{1}H- and ^{19}F-NMR spectra of **1b** at −30°. At higher temperature the solution darkened. When the reaction mixture was quenched at −78° with MeOH/HCl, a 1:2 mixture of methyl 1- and 2-naphthoate (**10** and **11,** respectively) was isolated.

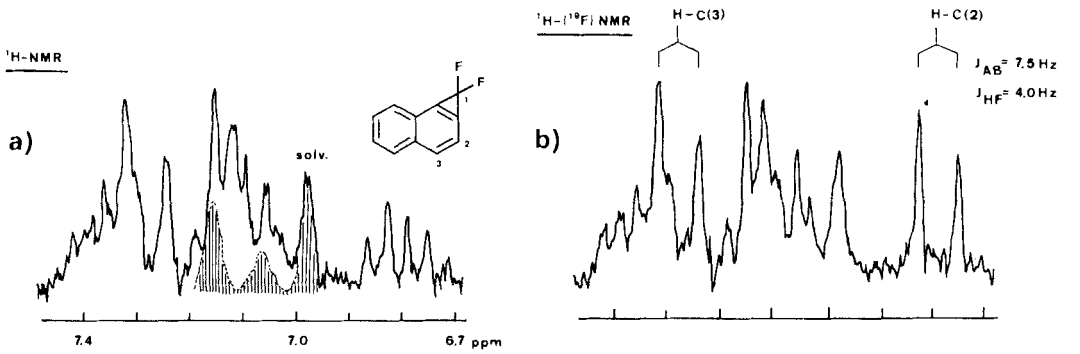


Figure. a) *^{1}H-NMR spectrum of* **1b** *in (D_8)toluene, −30°, at 100 MHz.* Sweep width 250 Hz. The shaded area corresponds to the solvent, recorded under identical conditions. b) *^{1}H-NMR spectrum of* **1c** (same conditions as in *a*) *with ^{19}F-heteronuclear decoupling.*

The ^{1}H-NMR spectrum of **1b** was recorded in (D_8)toluene at 100 MHz *(Figure)*. The aromatic protons constitute a complex multiplet from 6.7–7.5 ppm in which the lines assigned to H–C(2) and H–C(3) can be identified. The quintuplet at 6.7–6.9 ppm collapses to a doublet upon ^{19}F-heteronuclear decoupling (doublet, J(H,F) = 4.0 Hz, 87 ppm downfield from C_6F_6). It is therefore assigned to H–C(2). The resulting doublet is part of an *AB*-system with $^3J_{(AB)}$ = 7.5 Hz. Decoupling experiments carried out at 360 MHz show the lines of H–C(3) at 7.23 and 4.32 ppm. The vicinal coupling of 7.5 Hz is in good agreement with that of 6.9 Hz observed for **1** [2], while the ^{19}F chemical shift and ^4J(H,F) correspond to those of 1,1-difluoro-1*H*-cyclopropa[*b*]-naphthalene (δ = 80.3 ppm, ^4J(H,F) = 3.9 Hz) [9]. The ^{1}H-NMR spectrum of **1b** in (D_8)THF is shifted downfield by *ca.* 1 ppm with respect to that in (D_8)toluene; however, resolution problems prevented more detailed analysis of the pattern.

Financial support by the *Swiss National Science Foundation* (project No. 2.236-0.81) is gratefully acknowledged. We are indebted to Messrs. *J.-P. Saulnier* and *A. Pinto* for the NMR spectra.

Experimental Part

General. See [10].

*7b-Bromo-1,1-difluoro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene* (**8**). To a solution of **7** [6] (8.05 g, 38.5 mmol) in refluxing diglyme (65 ml) was added dropwise $ClF_2CCOONa$ [7] (60.32 g, 0.4 mmol) in dry diglyme (145 ml) at 170°. After addition heating was continued until evolution of CO_2 ceased (20 h). The cooled mixture was filtered through aluminium oxide. After evaporation of the solvent a 70°/12 Torr the residue was distilled and the fraction boiling at 78–123°/20 Torr purified by chromatography (silica gel) with toluene/petroleum ether 1:10. Yield 2.64 g (27%) of **8** (colourless oil). ^{1}H-NMR (360 MHz, $CDCl_3$): 2.98–3.09 (*m*, 1H); 3.16–3.30 (*m*, 1H); 3.36–3.48 (*m*, 1H); 3.56–3.72 (*m*, 1H); 3.83–3.97 (*m*, 1H); 7.08–7.15 (*m*, 1H); 7.18–7.37 (*m*, 2H); 7.68–7.73 (*m*, 1H). ^{19}F-NMR ($CDCl_3$): 30.91 (*AB*-system δ_A = 19.56, m; δ_B = 42.25, *m*; $^2J_{(AB)}$ = 144). MS: 258/260 (5, M^+), 229/231 (77), 179 (60), 164 (25), 159 (29), 151 (33), 129 (85), 128 (100).

*7b-Bromo-1,1-dichloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene* (**8a**). A solution of **7** (1.26 g, 6 mmol) and $PhHgCCl_3$ [11] (2.98 g, 7.5 mmol) in benzene (5.8 ml) was refluxed under N_2 during 92 h. The cooled solution was filtered, the filtrate concentrated and the residue purified by column chromatography (silica gel) with CH_2Cl_2. Yield 1.5 g (85%) of **8a** as colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.81–1.94 (*m*, 1H); 2.33–2.45 (*m*, 1H); 2.45–2.66 (*m*, 2H); 2.80–3.00 (*m*, 1H); 7.00–7.12 (*m*, 1H); 7.12–7.37 (*m*, 2H); 7.53–7.67 (*m*, 1H). MS: 290/292/294 (6, M^+), 262/264/266 (7), 255/257/259 (12), 211/213/215 (66), 183/185 (36), 177 (45), 176 (34), 175 (57), 129 (79), 128 (100), 127 (40), 126 (11).

*3,7b-Dibromo-1,1-difluoro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene* (**9**). Recrystallized *N*-bromosuccinimide (1.81 g, 10.2 mmol) and dibenzoyl peroxide (66 mg) were heated to reflux with **8** (2.64 g, 10.2 mmol) in CCl_4 (23 ml) during 20 min. The cooled solution was filtered and concentrated. Crystallization with hexane

furnished 1.62 g (47%) of **9**, m.p. 90–91°. ^{1}H-NMR (360 MHz, $CDCl_3$): 2.33–2.47 (*m*, 1H); 2.48–2.60 (*m*, 1H); 2.80–2.92 (*m*, 1H); 5.14 (*m*, 1H); 7.18–7.25 (*m*, 1H); 7.25–2.35 (*m*, 1H); 7.35–7.43 (*m*, 1H); 7.58–7.68 (*m*, 1H). ^{19}F-NMR ($CDCl_3$): 29.11 (*AB*-system, $\delta_A = 37.02$, *m*; $\delta_B = 21.20$, *m*, $^3J_{(AB)} = 143.5$). MS: 336/338/340 (*w*, M^+), 285/287/289 (*w*), 257/259 (9), 256/258 (25), 230/232 (10), 206/208 (4), 178 (42), 177 (100), 157 (10), 151 (14), 128 (49), 127 (17), 126 (8).

The same procedure applied to **8a** afforded *3,7b-Dibromo-1,1-dichloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene* (**9a**) (50%), m.p. 81–82°. ^{1}H-NMR (360 MHz, $CDCl_3$): 2.35–2.48 (*m*, 1H); 2.48–2.60 (*m*, 1H); 2.98–3.10 (*m*, 1H); 5.10 (*t*, $^3J = 3$, H–C(3)); 7.14–7.20 (*m*, 1H); 7.20–7.30 (*m*, 1H); 7.35–7.45 (*m*, 1H); 7.60–7.70 (*m*, 1H). MS: 368/370/372/374/376 (2, M^+), 289/291/293 (16), 288/290/292 (21), 262/264/266 (13), 253/255/257 (20), 210/212 (36), 209/211 (100), 183/185 (24), 175/177 (69), 139 (76), 128 (49). Anal. calc. for $C_{11}H_8Br_2Cl_2$ (370.91): C 35.62, H 2.17, Br 43.09, Cl 19.12; found: C 35.95, H 2.22, Br 42.25, Cl 19.47.

*1,1-Difluoro-1*H*-cyclopropa[*a*]napthalene* (**1b**). To 60 mg of **9** in dried THF (0.3 ml) at −78° was slowly added under Ar a solution of *t*-BuOK (80 mg, 0.71 mmol) in THF (1 ml). After addition the solution was warmed to −35° and the THF was evaporated at −35°/0.5 Torr during 90 min. The residue was cooled to −78° and treated with (D_8)toluene (1 ml). Part of the solution was filtered through a filter disk into a pre-cooled NMR tube. After sealing of the tube and ^{1}H- and ^{19}F-NMR spectra were recorded at −30° on a *Varian XL-100* instrument (see the *Figure*).

Methanolysis of **1b.** After recording of the NMR spectra the content of the NMR tube was treated at −78° with a solution of MeOH (3 ml) and conc. HCl (0.1 ml). The mixture was stirred at r.t. for 15 h. After usual workup the crude product was purified by chromatography (silica gel) with toluene/$CHCl_3$ 9:1 to afford 6.9 mg (20%) methyl 1-naphthoate (**10**) and 14.3 mg (43%) of methyl 2-naphthoate (**11**). Both products were identified by comparison of their spectral properties with samples prepared by esterification of the corresponding naphthoic acids.

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