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1,1-DIHALOGENONAPHTHO[b]CYCLOPROPENES

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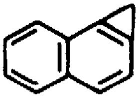
Summary. The synthesis of 1,1-dichloro- and 1,1-difluoronaphtho[b]cyclopropene is described, starting from 4,5-dimethylenecyclohexene and the respective tetrahalogenocyclopropenes.

Over the recent years the isomeric naphto[a]cyclopropene (1)[1] and naphtho[b]cyclopropene (2)[2] as well as the even more strained homologues 3[3] and 4[4] have been described. The only functionalized naphthocyclopropene known is the 1,1-dichloro-2,7-diphenyl derivative 5 which has been synthesized by Halton in 1972[5] from *trans*-1,2-diphenylbenzocyclobutene (6) and tetrachlorocyclopropene (7). We now report the syntheses of 1,1-dichloro- and 1,1-difluoronaphtho[b]cyclopropenes 8 and 9. Our scheme follows closely the sequence used by Halton for preparation of 5.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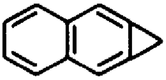
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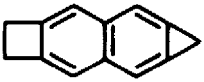
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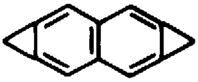
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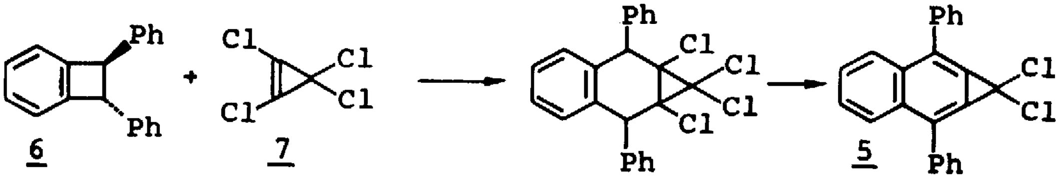
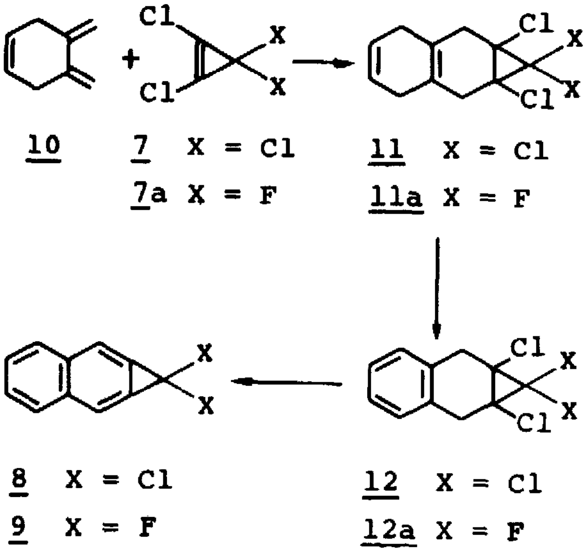


However, since preliminary experiments showed that benzocyclobutenes lacking substituents in positions 1 and 2 would not undergo cycloaddition to tetrachlorocyclopropene, the desired ring system was constructed from 4,5-dimethylenecyclohexene (10)[6] and the corresponding cyclopropene derivative 7 and 7a[7] respectively:



Cycloaddition of 10 to 7 in CCl_4 in the presence of sodium bicarbonate (25°, 3d) afforded the adduct 11[8] in 87% yield. Conversion 11 → 12 was effected in 94% yield with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in CCl_4 (25°, 3h). Exposure of 12 to an excess of KO*t*Bu in THF (-70 to -20°) followed by anhydrous work-up[10] and sublimation at 40° *in vacuo* afforded 1,1-dichloronaphtho[b]cyclopropene (8) (m.p. 94-97° d) in 66% yield. The ^{1}H-NMR spectrum of 8 (Fig. 1) consists in the expected AA'BB' system for the less perturbed benzene ring and a singlet for the protons of the central ring. The spectrum resembles that of the parent hydrocarbon, the main difference being a stronger downfield shift by 0.6 ppm of H(2,7) in 8. In the ^{13}C-NMR the signals appear at 59.0 (C-1), 129.8 (C-1a,7a), 113.5 (C-2,7), 138 (C-2a,6a), 129.8 (C-3,6), and 127.9 (C-4,5) ppm. These assignments, as those of the difluoro derivative 9, are tentative and will be confirmed experimentally.

Similarly, cycloaddition of dimethylenecyclohexene (10) to 7a as described above (6 days at 25°, + 4 d at 40°) afforded a *ca.* 2:1 mixture of 11a[11] and 12a[12] which upon treatment with DDQ was converted in 45% overall yield to 12a. Aromatization with KO*t*Bu in THF, followed by column chromatography on silica gel gave a 70% yield of 1,1-difluoronaphtho[b]cyclopropene (9).
In the ^{1}H-NMR of 9 H(2,7) resonate at 8.02 ppm (t, $J_{H,F}$ = 3.9 Hz, Fig. 2). The corresponding triplet in the ^{19}F-NMR appears at 80.3 ppm downfield from C_6F_6.[13] The ^{13}C resonance lines,

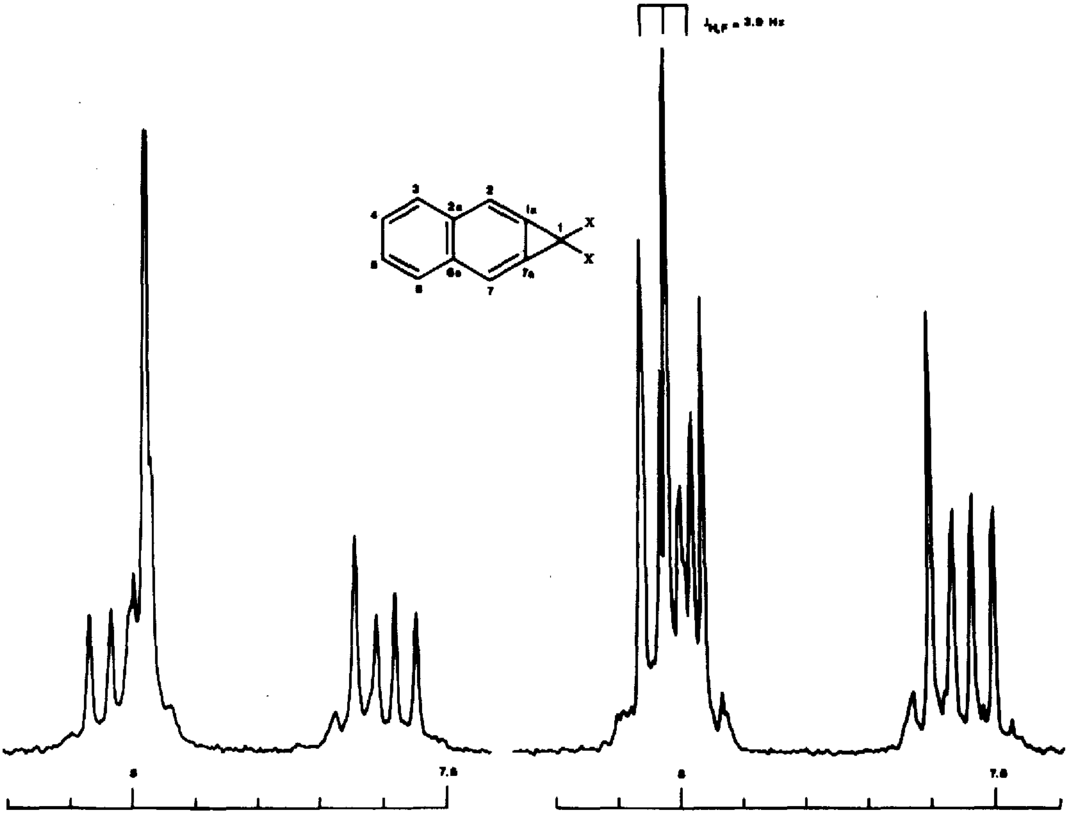
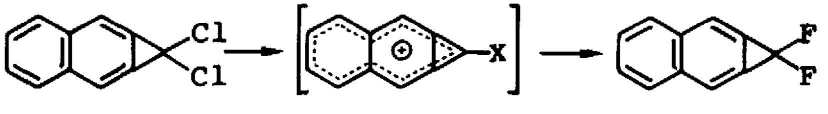


Fig. 1 ^{1}H-NMR spectrum of 8 (X = Cl)

Fig. 2. ^{1}H-NMR spectrum of 9 (X = F)

assigned on the grounds of magnitude of C,F coupling constants and H-decoupling experiments, are found at 101.7 (C-1, $J_{C,F}$ = 307 Hz), 125.1 (C-1a,2a, $J_{C,F}$ = 20 Hz), 115 (C-2,7), 138.5 (C-2a,6a, $J_{C,F}$ = 2.5 Hz), 130 (C-3,6), and 128 (C-4,5).

From our present knowledge, the chemistry of 1,1-dihalogenonaphtho[b]cyclopropenes is related to that of the corresponding 1,1-dihalogenobenzocyclopropenes. Thus the dichloro derivative 8 is converted to the difluoro compound 9 upon treatment with AgF in CH_3CN.[14] A halogenonaphthocyclopropenium ion 13 is the most likely intermediate in this exchange. Experiments towards spectroscopic investigation of 13 are under way in this laboratory.



8 **13** X = Cl or F **9**

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REFERENCES AND NOTES

1) W.E. Billups & W.Y. Chow, J. Am. Chem. Soc. 95, (1973); W.E. Billups, W.Y. Chow, K.H. Leavell, E.S. Lewis, J.L. Margrave, R.L. Sass, J.J. Shieh, P.G. Werness & J.L. Wood, *ibid.* 95, 7878 (1973).

2) S. Tanimoto, R. Schäfer, J. Ippen & E. Vogel, Angew. Chem. 88, 643 (1976); Angew. Chem. Int. Ed. Engl. 15, 613 (1976).

3) D. Davalian & P.J. Garratt, Tetrahedron Letters 1976, 2815.

4) J. Ippen & E. Vogel, Angew. Chem. 86, 780 (1974); Angew. Chem. Int. Ed. Engl. 13, 736 (1974)

5) A.R. Browne & B. Halton, J. Chem. Soc., Chem. Commun. 1972, 1341.

6) E.D. Middlemas & L.D. Quin, J. Org. Chem. 44, 2587 (1979).

7) J. Sepiol & R.L. Soulen, J. Org. Chem. 40, 3791 (1975).

8) ^{1}H-NMR (δ) of 11 (m.p. 69-73); 2.46 (s broad, 4H), 2.86 (s broad, 4H), 5.59 (m, 2H).

9) ^{1}H-NMR (δ) of 12 (m.p. 111-113); 3.63 (s, 4H), 7.05 (s, 4H).

10) P. Müller, R. Etienne, J. Pfyffer, N. Pineda & M. Schipoff, Helv. Chim. Acta 61, 2482 (1978)

11) ^{1}H-NMR (δ) of 11a: 2.5 (s broad, 4H), 2.7 (d, J = 4 Hz, 4H), 5.6 (s broad, 2H). ^{19}F-NMR: AB system (J_{AB} = 151 Hz) at 24.75 ppm downfield from C_6F_6; δ_A = 31.8, δ_B = 17.7 ppm.

12) ^{1}H-NMR (δ) of 12a: 3.46 (d, J = 3, 4H), 7.1 (s broad, 4H). ^{19}F-NMR: AB system at 29.65 ppm (J_{AB} = 156 Hz) downfield from C_6F_6; δ_A = 34.96, δ_B = 24.34 ppm.

13) In 1,1-difluorobenzocyclopropene and 1,1-difluoro-2,5-diphenylbenzocyclopropene the corresponding signals appear at 80.9 and 79.9 ppm respectively.

14) P. Müller, J. Chem. Soc., Chem. Commun. 1973, 895.

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