33. 1,1-Dihalogenoanthra[*b*]cyclopropenes

Preliminary communication[1])

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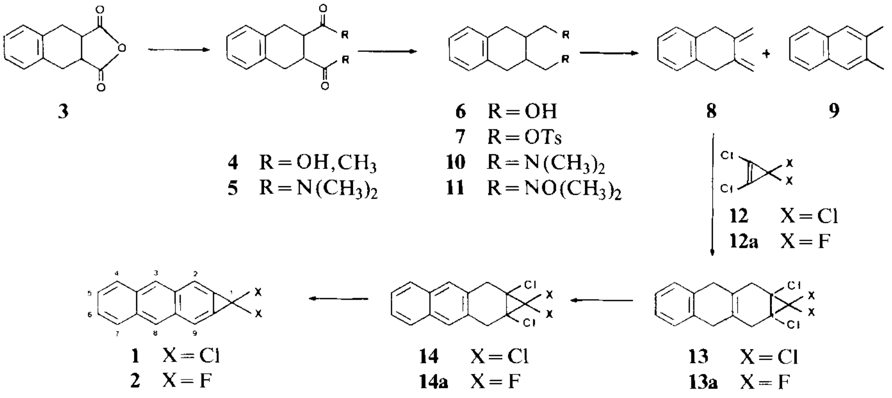
Summary

1,1-Dichloro- and 1,1-difluoroanthra[*b*]cyclopropene (**1** and **2**) are synthesized in 8 steps from the *Diels-Alder* adduct of benzocyclobutene and maleic anhydride.

Although the chemistry of the highly strained benzo- [1] and naphthocyclopropenes [2] is well established, the benzannelated homologues have so far remained elusive. To our knowledge, the only reports deal with the attempted synthesis of anthra[*b*]cyclopropene *via* the *Billups* [3] route. We describe the synthesis of the dichloro- and difluoroanthra[*b*]cyclopropenes **1** and **2** by a straightforward extension of our reported sequence for preparation of 1,1-dihalogenonaphtho[*b*]cyclopropenes [4]. The *Diels-Alder* adduct **3** [5] of benzocyclobutene [6] and maleic anhydride *(Scheme)* was hydrolyzed in boiling methanol to the diester **4**. Reduction with $LiAlH_4$ afforded the diol **6** which was converted to the ditosylate **7**. Unfortunately, elimination with *t*BuOK in THF did not give the desired diene **8**, but almost exclusively 2,3-dimethylnaphthalene (**9**). Although a variety of elimination procedures were tried, the base-catalyzed

Scheme



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[1]) The full paper will be published in Helv.

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aromatization to **9** could not be suppressed. An approach *via* thermal elimination was tried, using the methodology described for the preparation of 4,5-dimethylidenecyclohexene [7]. The diacid **4** was converted to the diamide **5** with hexamethylphosphorous amide in 95% yield. Reduction with $LiAlH_4$ gave the diamine **10** (90%) which was oxidized to the *N*-oxide **11**. The latter was pyrolyzed without purification at 180°/10^{-2} Torr to give 1,2,3,4-tetrahydro-2,3-dimethylidenenaphthalene (**8**) [20-30%; ^{1}H-NMR.: 7.0 (*s*), 5.26 and 4.83 (*m*, vinylic H), 3.45 (*m*, aliphatic H)]. *Diels-Alder* addition of **8** to tetrachlorocyclopropene (**12**) in presence of $NaHCO_3$ proceeded at RT. in 40 h (62%). Similarly, with 1,2-dichloro-3,3-difluorocyclopropene (**12a**) [8] the adduct **13a** was formed in 22% yield after 6 days at 45°. Dehydrohalogenation to **1** and **2** was carried out with 2.2 mol-equiv. of *t*BuOK in THF at −70° to 25°, followed by anhydrous work-up. 1,1-Dichloroanthra[*b*]cyclopropene (**1**) was obtained in *ca.* 70% yield together with some unreacted **13**. The compound showed a strong tendency to decompose, and could not be isolated pure. However, its structure could be deduced unambiguously from its ^{1}H-NMR. spectrum *(Fig. 1)* and from the spectrum of the difluoro derivative **2** *(Fig. 2)*. The latter compound, which was formed in 88% yield had m.p. 192-194° (from $CHCl_3$).

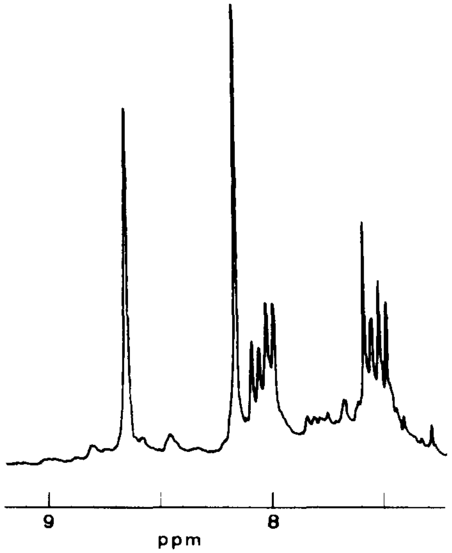

Fig. 1. *^{1}H-NMR. spectrum of 1,1-dichloroanthra[*b*]cyclopropene* (**1**)

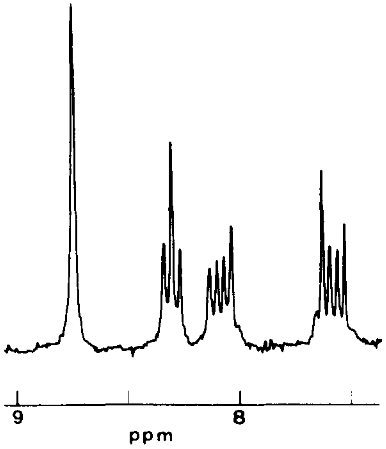

Fig. 2. *^{1}H-NMR. spectrum of 1,1-difluoroanthra[*b*]cyclopropene* (**2**)

The MS. showed main peaks at *m/z* 226 (100, M^+); 207 (16, $M^+ - F$); 176 (19, $M^+ - CF_2$). The ^{1}H-NMR. spectrum *(Fig. 2)* displays the expected pattern with the *AA'BB'*-system of the H-atoms at C(4)–C(7); the triplet at 8.31 ppm is due to H–C(2, 9) (J(H,F) = 3.75 Hz) and the singlet at 8.75 to H–C(3, 8). In the ^{19}F-NMR. spectrum the corresponding triplet is found at 77.6 ppm downfield from C_6F_6. The ionization of dihalogenoanthra[*b*]cyclopropenes to form aromatic cations and the reduction to unsubstituted hydrocarbons is currently under investigation.

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