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8,11-DICHLORO[5]METACYCLOPHANE

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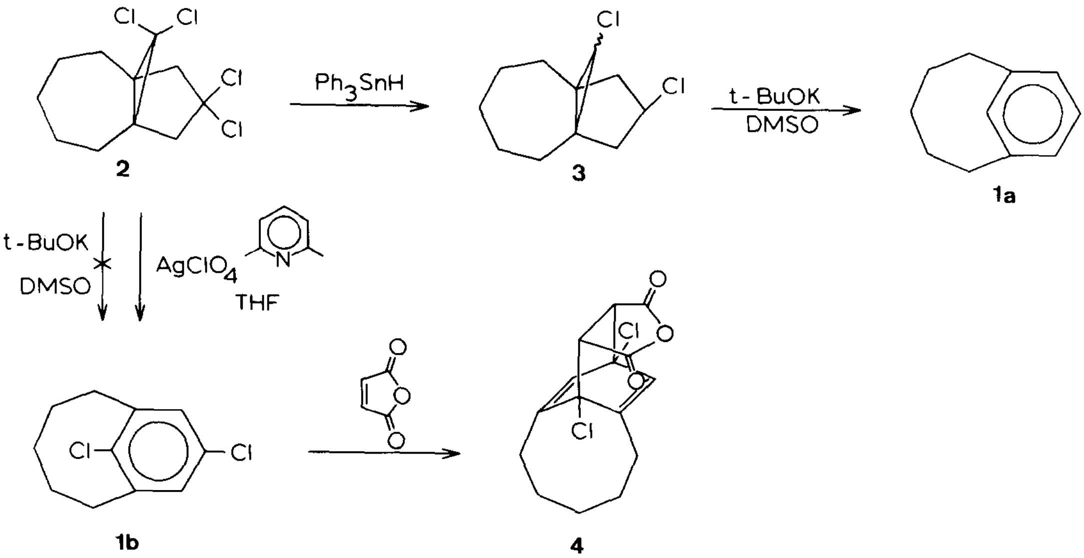
Abstract: The title compound 1b was prepared by treating the tetrachloropropellane 2 with $AgClO_4$/2,6-lutidine in THF. Towards protons and dienophiles, 1b is less reactive than the unsubstituted 1a.

Recently, we described the synthesis of [5]metacyclophane (1a) from the tetrachloropropellane 2 via 3 in 30% yield[1] (Scheme 1). The synthesis of 1b, the 8,11-dichloro-derivative of 1a, was of interest for the following reasons. In the first place, 3 still forms a bottleneck in the synthesis of 1a, as it has to be isolated by preparative GLC and on transformation to 1a yields considerable amounts of isomeric byproducts. If 1b was obtained in good yield, its reduction would open an alternative route to 1a. Furthermore, it was hoped that 1b or a crystalline derivative prepared therefrom would allow a X-ray crystal structure determination. This was desirable in order to confirm the interesting structure of 1a, the shortest known benzenoid metacyclophane[2]; its spectral[3,4] and chemical[5] properties as well as MNDO calculations[4] indicate 1a to be a highly strained molecule with a non-planar benzene ring.

The approach successfully applied for the synthesis of 1a did not work for 1b: treatment of 2 with t-BuOK in DMSO gave no identifiable products. However, the method used by Grice and Reese[6] for the synthesis of 7,8-benzo-11-chloro[5]metacyclophane gave good results in our case: the reaction of 2 with $AgClO_4$ in the presence of 2,6-lutidine in THF solution yielded 1b (preparative GLC; 80%),which in very pure form gives colourless crystals of m.p. 40-42 °C.Its structure was assigned on the basis of its spectral[7] and chemical properties (Scheme 1 and 2). In particular, the ultraviolet spectrum of 1b in cyclohexane (λ_{max} = 272, 326 nm; $\varepsilon_{272} : \varepsilon_{326} = 20$) reveals the effect of distortion of the benzene ring if compared with that of 1,4-dichlorobenzene (in isooctane : λ_{max} = 225, 273 nm; $\varepsilon_{225} : \varepsilon_{273} = 25$; no end absorption above 300 nm)[8]; a comparable shift has been observed for 1a[3] (λ_{max} = 306.5 nm; m-xylene : λ_{max} = 262.5 nm).

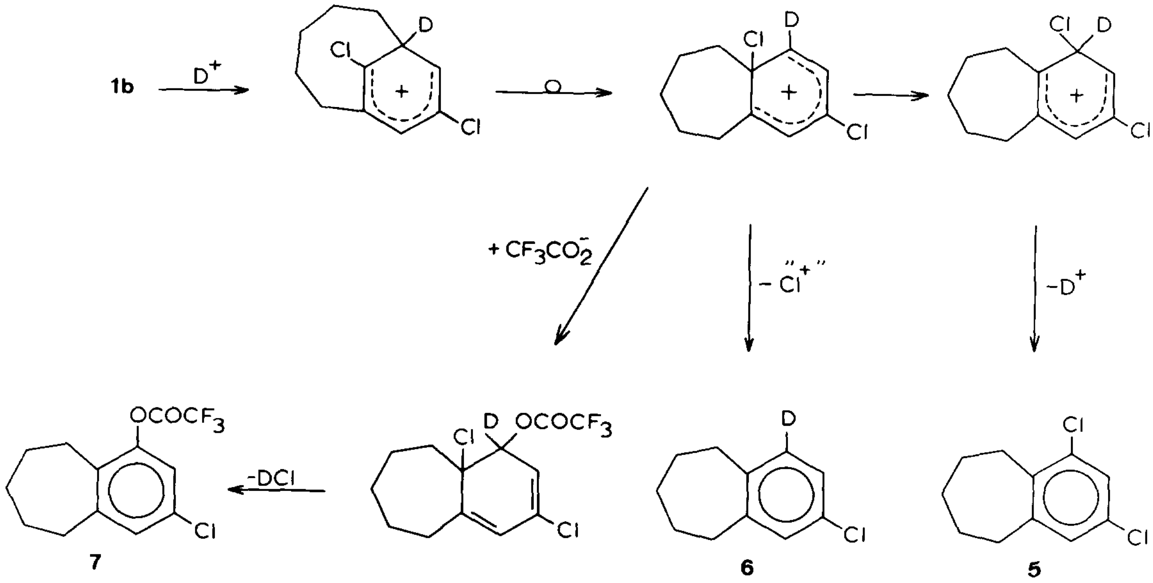
Scheme 1



The chemical reactivity of 1b was strongly reduced compared to that of 1a. With maleic anhydride in $CDCl_3$ at room temperature, 1a reacted in less than 15 min to give the Diels-Alder adduct[5]; the corresponding reaction of 1b to yield 4[9] has a half life of 3 h. Similarly, the acid catalyzed rearrangement of 1a to its ortho-isomer benzocycloheptene was instantaneous, but for 1b with CF_3COOD in $CDCl_3$ at room temperature, 3 h were needed for complete reaction. The main product of this reaction was 5[10] (70% yield); amongst about 10 byproducts, 6 and 7 were tentatively identified by GCMS[11] and by the mechanistic considerations reflected in Scheme 2 (cf. also ref. 6).

The relative stability of 1b towards protons and dienophiles may be explained by the electron withdrawing effect of the chlorine substituents. More surprising was its rather high thermal stability. When heated in a sealed ampoule in dry C_6D_6 to 184°C for 51 h, more than 50% of 1b was recovered; ca. 10% 5 was formed, while the remaining products were of higher molecular weight (MS). In contrast, 1a cleanly rearranged to benzocycloheptene at 150°C in DMSO-d_6[3], and at 185°C in cyclohexane-d_{12} (half life ca. 40 h). This rearrangement has been proposed to occur via a benzvalene intermediate[3]. However, as 1b is probably sterically more hindered than 1a, one would expect it to be more reactive if the process is purely thermal and uncatalyzed. On the other hand, the higher reactivity of 1a parallels its greater sensitivity in the acid catalyzed rearrangement; it is therefore not impossible that the "thermal" rearrangement of 1a and 1b is in reality catalyzed by traces of water (which were excluded by special precautions to the best of our knowledge) or by acidic centers in the ampoule glass wall. Only labelling experiments will be able to decide between the two possibilities.

Scheme 2



Some of our initial goals - reduction of 1b to 1a and synthesis of a crystalline derivative - have not been realized so far. Treatment of 1b with n-BuLi in Et_2O/hexane, with sodium in liquid ammonia, or with lithium in t-BuOH[12] gave, according to the NMR spectra, complex mixtures of products. The bromine analogue of 1b is expected to be more reactive in metallation reactions[13]; its synthesis is being investigated. The fact that 1b is a low-melting solid has so far hampered our attempts to obtain crystals suitable for X-ray structure determination; however, these attempts will be continued.

References and Notes

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6. P. Grice and C.B. Reese, *J. Chem. Soc. Chem. Commun.*, **1980**, 424.
7. A detailed discussion of the ^{1}H NMR spectrum is presented in ref. 4. **1b**: mass spectrum:m/z= 214 $[C_{11}H_{12}{}^{35}Cl_2]^{+\cdot}$ 39%, found 214.0322, calc. for $M^{+\cdot}$ 214.0316; 179 $[C_{11}H_{12}{}^{35}Cl]^+$ 100%.
8. Ultraviolet Spectral Data, API Research Project 44, no. 460.
9. **4**: ^{1}H NMR (90 MHz, $CDCl_3$, δ in ppm): 6.20 (s, 1H), 6.06 (s, 1H), 3.69 (s, 2H), 3.1-0.8 (m, 10H); cf. the ^{1}H NMR spectrum of chlorine-free parent compound[5].
10. **5**: ^{1}H NMR (90 MHz, $CDCl_3$, δ in ppm): 7.21, 7.00 (q, AB, J_{AB} = 2.5 Hz, 2H), 3.09-2.60 (m, 4H), 2.07-1.44 (m, 6H). Mass spectrum:m/z (%) 218 (6), 216 (33), 214 (55), $[C_{11}H_{12}Cl_2]^{+\cdot}$ = $[\mathbf{5}]^{+\cdot}$; 181 (33), 179 (100), $[\mathbf{5}\text{-}Cl]^+$; 176 (5), 174 (27), 172 (42), $[\mathbf{5}\text{-}C_3H_6]^{+\cdot}$; 115 (37).
11. **6**: Mass spectrum:m/z (%) 183 (10), $[C_{11}H_{12}{}^{37}ClD]^{+\cdot}$, 182 (11), 181 (41) $[C_{11}H_{12}{}^{35}ClD]^{+\cdot}$ = $[\mathbf{6}]^{+\cdot}$, 180 (26), 146 (100) $[\mathbf{6}\text{-}Cl]^+$, 145 (85) $[\mathbf{6}\text{-}HCl]^{+\cdot}$, 141 (12), 139 (30) $[\mathbf{6}\text{-}C_3H_6]^{+\cdot}$. **7**: Mass spectrum:m/z (%) 294 (28) $[C_{13}H_{12}{}^{37}ClF_3O_2]^{+\cdot}$, 292 (100) $[C_{13}H_{12}{}^{35}ClF_3O_2]^{+\cdot}$ = $[\mathbf{7}]^{+\cdot}$, 263 (18), 257 (66), $[\mathbf{7}\text{-}Cl]^+$, 252 (17), 251 (19), 250 (59) $[\mathbf{7}\text{-}C_3H_6]^{+\cdot}$, 181(15), 180 (10), 179 (41) $[\mathbf{7}\text{-}CF_3COOH]^{+\cdot}$
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