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SYNTHESIS AND MECHANISM OF FORMATION OF 2-HALOBENZOCYCLOPROPENES FROM TETRAHALOBICYCLO(4.1.0)HEPTANES

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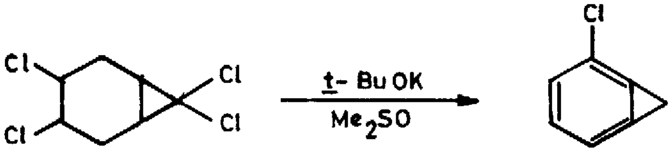
Although a study on the synthesis and mechanism of formation of strained benzocyclopropene[1,2] from 7,7-dichlorobicyclo(4.1.0)hept-3-ene has been reported, 2- or 3-halobenzocyclopropene is unknown.[3] We now wish to report here the first synthesis of 2-chlorobenzocyclopropene (2), and the mechanistic study of its formation from 3,4,7,7-tetrachlorobicyclo(4.1.0)heptane (1).[4]

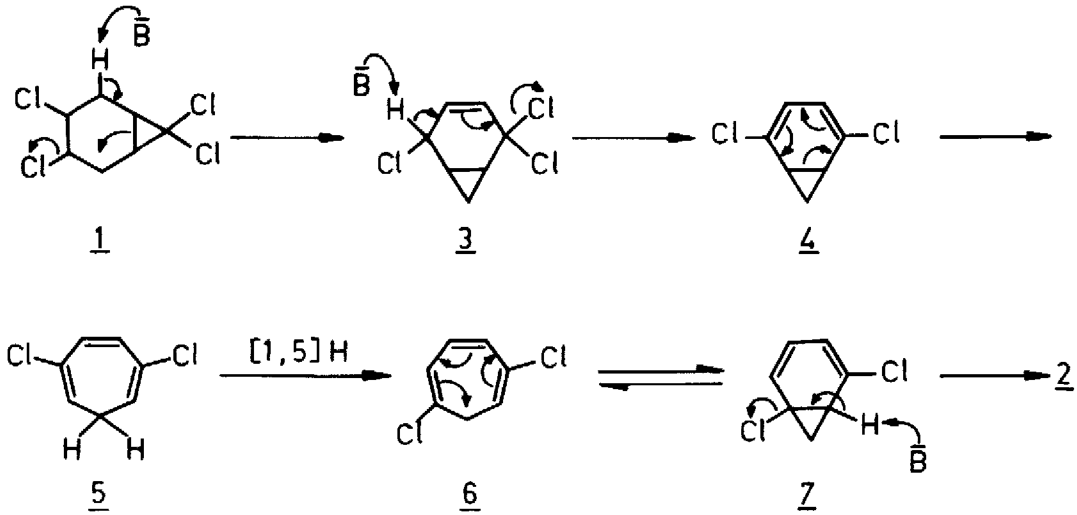


1　　　　　　　　2

Treatment of 1 with a four fold excess of chilled solution of t-BuOK in DMSO for one hr and purification by high vacuum distillation gave 2 in *ca*. 50% yield (purity > 95% by GLC). The structural assignment of 2 was based on its elemental analyses and spectral properties: Anal. Calcd for C_7H_5Cl: C, 67.47; H, 4.01. Found: C, 67.45; H, 4.05; IR (neat): ν_{max} = 1680 (aromatic double bond), 830 and 740 (aromatic) cm^{-1}; UV (C_2H_5OH) λ_{max} = 242 (log ε 3.27), 250 (log ε 3.34), 258 (log ε 3.38), 266 (log ε 3.32) and 270 (log ε 3.24) nm; NMR (CCl_4); δ3.26 (s, 2H), 7.10 (dd, 1H), 7.14 (d, 1H) and 7.18 (d, 1H); and MS: m/e ions at 124 and 126 in the ratio 3:1. We have also synthesized and characterized 2-bromobenzocyclopropene[5] from 3,4,7,7-tetrabromobicyclo(4.1.0)heptane.[5]

We suggest the mechanism shown in Scheme for the formation of 2 from 1. The driving force for the reaction may be the relief of strain gained by the formation of 5 which can give rise to 6 by 1,5-H shift. Under the reaction conditions, 6 can undergo ready dehydrochlorination *via* 7 to form 2.

Scheme



Furthermore, a similar dehydrochlorination of 3,4,7-trichlorobicyclo(4.1.0)-heptane[5] using t-BuOK gave benzocyclopropene.[1] In support of the proposed mechanism we carried out a control dehydrochlorination of 3,4,7-trichlorobicyclo(4.1.0) heptane which allowed us to isolate and characterize the intermediate 2-chloro-1,3,5-cycloheptatriene.[6] In addition, the isolated intermediate on further treatment with the base provided benzocyclopropene[1] thereby confirming the proposed pathway of this interesting selective transformation.

At present the obvious synthetic utility of the new route for the synthesis of other 2-substituted benzocyclopropenes is being studied.

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