Tetrahedron Letters, Vol.22, No.37, pp 3687 - 3688, 1981
Printed in Great Britain

0040-4039/81/373687-02$02.00/0

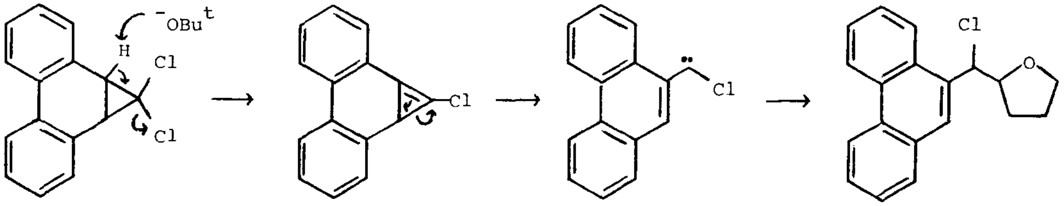
DEHYDROHALOGENATION OF *endo*-1-CHLORO-1a,9b-DIHYDROCYCLOPROPA[ℓ]PHENANTHRENE

Brian Halton* and David L. Officer

Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand.

Summary: *Base induced dehydrochlorination of the title compound (4) leads to products by way of the Δ^1-olefin (5). Under solvolytic conditions the dibenzcycloheptatriene (9) is produced.*

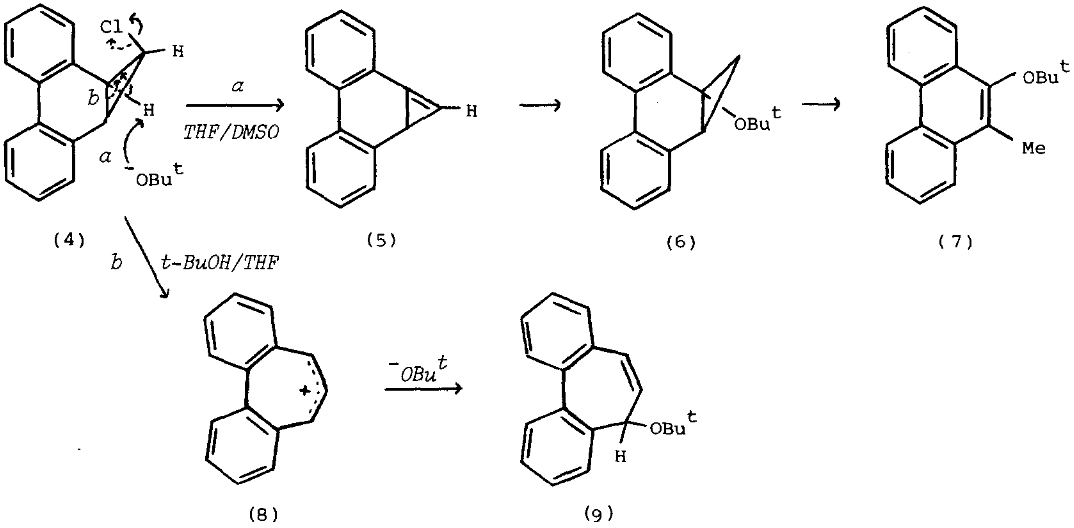
The recent report by Billups and his co-workers on the generation of bicyclo[4,1,0]hepta-2,4,6-trienes[1] prompts us to report our findings in this area. As part of a continuing programme aimed at the synthesis and chemistry of the cycloproparenes,[2] we have examined the dehydrochlorination of appropriately functionalised dihydrocyclopropa[ℓ]phenanthrenes, e.g. (1) and (4), as a possible route to the as yet unknown[2,3] aromatic species.



(1) (2) (3)

Scheme 1

We concur with the U.S. group[1,4] that dehydrochlorination of (1) leads to the formation of the solvent incorporated product (3) by way of the bicyclo[4,1,0]heptatriene (2) (Scheme 1). We also agree that the half-reduction product (4)[5] is unreactive towards potassium t-butoxide in tetrahydrofuran (THF) since unchanged starting material is returned in yields of up to 90%. However, in our hands the use of 2 molar equivalents of the base in dimethyl sulphoxide (DMSO) results in severe decomposition of (4) and the formation of a complex, and as yet unresolved, mixture of *c.* 16 components (tlc). Since the precise nature of the base is a function of the medium in which it is used (potassium t-butoxide is tetrameric in THF but probably monomeric in DMSO),[6] a reactivity between the two extremes recorded above can be envisaged for (4) if a mixed solvent system is employed for the base. In the event, with a mixture of THF and DMSO (*c.* 1:2) significantly less discolouration ensues and a bright yellow oily solid is obtained on work up after 24 h at room temperature. The application of preparative tlc methods leads to unchanged starting material (4) (32%) and two colourless oils. The first of these is identified[7] as 1a-t-butoxy-1a,9b-dihydrocyclopropa[ℓ]phenanthrene (6) (3%) primarily from the appearance of an AMX-system in the ^{1}H nmr spectrum (δ: 0.7, m, *endo*-H1; 1.7, m, *exo*-H1; 2.8, m, H9b). The formation of a 1a-substituted derivative is fully compatible with nucleophilic



Scheme 2

capture of the triene (5) (path a, Scheme 2) as has been discussed for the analogue (2).[1,4] The second oil, while pure by analytical tlc, displays nmr resonances compatible only with a mixture of compounds, the major component of which is believed to be 9-t-butoxy-10-methylphenanthrene (7) (*c.* 4%) formed by rearrangement and aromatization of (6).

Under solvolytic conditions (THF-t-BuOH 2:1; elevated temperatures) the *endo*-chloro compound (4) is also susceptible to t-butoxide. In this case, in addition to recovered starting material (48%), 7-t-butoxydibenz[*a*,*c*]cyclohepta-1,3,5-triene (9) (18%)[7] is isolated and displays doublet resonances at 140.0 and 69.1 ppm for the C5 and C7 carbon atoms. The formation of (9) presumably involves cyclopropyl-allyl rearrangement and nucleophilic capture of the cycloheptatrienyl cation (8) thus formed (path b, Scheme 2). Hence in this context also, the *endo*-chloro derivative (4) behaves in an analogous way to its dichloro counterpart (1).[5]

Acknowledgements: Financial assistance from Victoria University and the New Zealand Universities Grants Committee is gratefully acknowledged.

References and Footnotes:

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(Received in UK 2 July 1981)