Tetrahedron Letters, Vol.22, No.34, pp 3317 - 3320, 1981
Printed in Great Britain

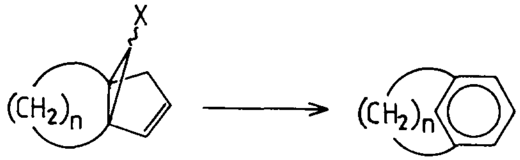
0040-4039/81/343317-04$02.00/0

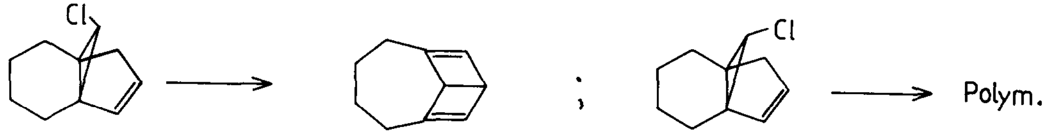
STUDIES ON THE FORMATION OF [5]METACYCLOPHANE

L.A.M. Turkenburg, P.M.L. Blok, W.H. de Wolf and F. Bickelhaupt*
Vakgroep Organische Chemie, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract: Base induced elimination of HCl from the dichloro[5.3.1]propellane 3a gives a mixture of [5]metacyclophane (1) and tetrahydrocyclopentacyclooctenes (2), while the stereoisomeric 3b affords 1 quantitatively.

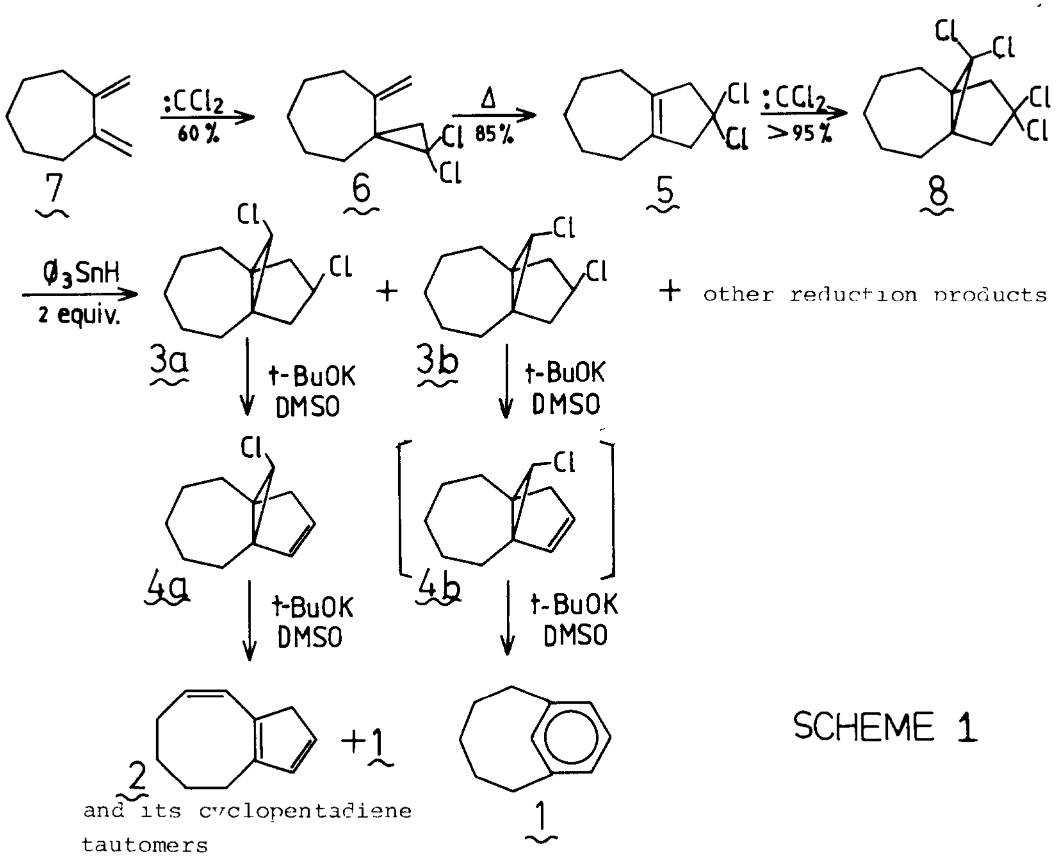
Recently, we reported that suitable halo[n.3.1]propellenes can be converted by base-induced elimination to short-bridged metacyclophanes (n=5,6)[1], or to the analogous Dewar isomer (n=4)[2].





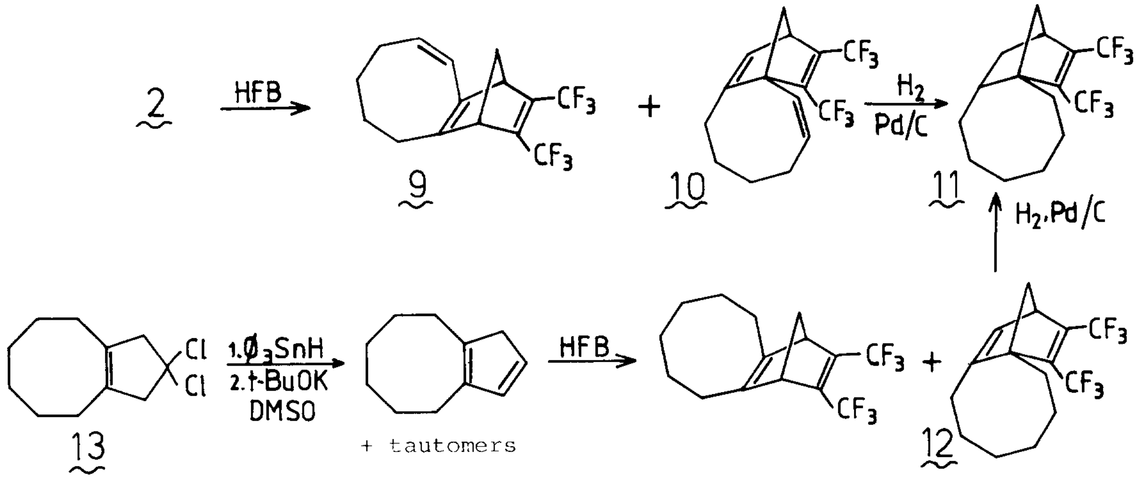
In the latter case the course of the reaction depends remarkably on the stereochemistry of the chloro substituent; therefore we decided to investigate the influence of the stereochemistry of the halogen in the synthesis of [5]metacyclophane (1). Contrary to our initial expectations, the reactions in the two closely related, homologous series take a rather different course; no Dewar isomer of 1 was obtained, but 1 and tetrahydrocyclopentacyclooctenes (2) instead (Scheme 1)

The elimination reactions were carried out with 3, the dichloropropellanes which are functional equivalents of the corresponding chloropropellenes 4. The rational synthesis of 3, incidentally, opens a practical preparative route to 1. The bicyclic precursor 5 was obtained by flow pyrolysis[3] (N_2; 285°C) of the mono-addition product (6) of dichlorocarbene[4] to 1,2-dimethylenecycloheptane (7)[5]; dichlorocarbene addition[6] to 5 gave 8, which was reacted with 2 equivalents of triphenyltin hydride[7] to give a mixture of products, from which the main components 3a and 3b were isolated by preparative g.l.c. (1.5 m, 10% Carbowax-20M on Chromosorb-WH, 150°C). The stereochemical assignment of 3a and 3b was based on the close resemblance of their NMR-spectra[8] with those of analogous compounds in the [4.3.1]propellane series, for which the stereochemistry was unambiguously determined by X-ray crystallography.[2]



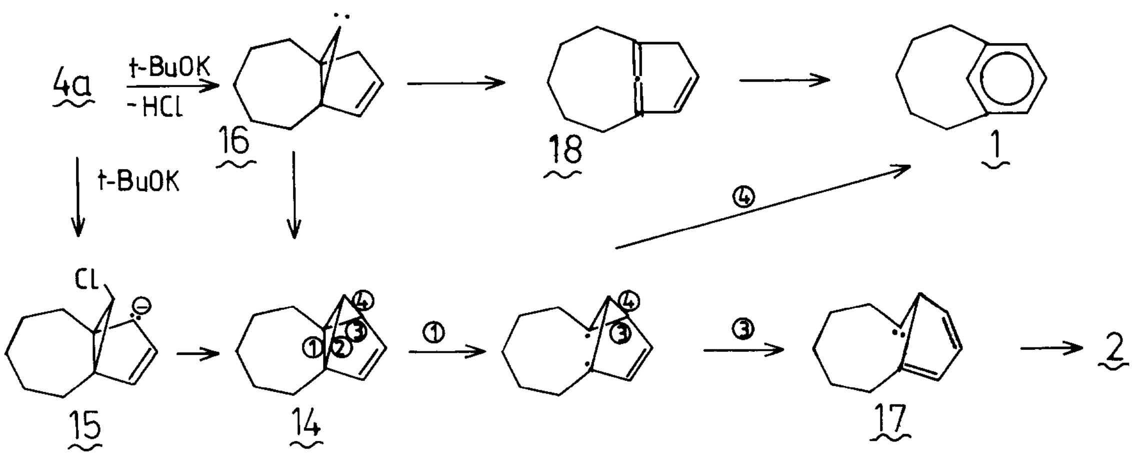
SCHEME 1

Treatment of 3a with 1 equivalent t-BuOK in DMSO at room temperature for 16 hours gave 4a which on treatment with an excess of the base, gave a mixture of 1 and 2 (ratios 25°C/16 h 1:3; 40°C/4 h ca. 3:2). When 3b was reacted with an excess of t-BuOK under the same reaction conditions as 3a, 1 was formed as the only product in nearly quantitative yield;even with less base no traces of 4b could be detected. According to the ^{13}C NMR spectrum, 2 is a mixture of at least 2 isomers, probably rapidly equilibrating by 1,5-hydrogen shifts. For the same reason, 2 could not be separated by g.l.c.: only one peak with the NMR spectrum of the mixture was observed. The structure assignment of 2 is mainly based on their Diels-Alder adducts with hexafluorobut-2-yne (HFB); the adducts were obtained ($CHCl_3$, 25°C, 1 h) as a mixture of three isomeric compounds. The two main products, 9 (30%) and 10 (60%) were separated by g.l.c. and identified by their NMR[8] and mass spectra; additional proof for the structure of 10 was obtained from its partial hydrogenation to 11; 11 was identical with the hydrogenation product of 12 which was synthesized by an independent route from 13 (cf. 5).(Scheme 2).



SCHEME 2

The exclusive formation of 1 from 3b can easily be understood; the first and rate determining step is presumably formation of 4b; deprotonation of 4b at the allylic position followed or accompanied by fast loss of chloride and disrotatory opening of the cyclopropane ring in accord with the Woodward-Hoffmann-DePuy rule[9] leads to 1. The interpretation of the transformation from 4a to 1 and 2 is less straightforward. In the first place, both products are completely different from the Dewar benzene found as the sole product from the lower homolog of 4a[2]. It is conceivable that benzvalene 14 is an intermediate; it could be formed from 4a via either the allylic anion 15 or the carbene 16[10] Cleavage of bonds ① and ④ would lead to 1, while cleavage of bonds ① and ③, equivalent to a "retro carbene reaction"[11,12] would lead to carbene 17 which by CH-insertion (directly or via a fulvene[13]) can react to furnish 2. An alternative route from 16 to 1 could proceed via the highly twisted allene 18



SCHEME 3

References and Notes

1. J.W. van Straten, W.H. de Wolf and F. Bickelhaupt, Tetrahedron Letters, 1977, 4667.
2. L.A.M. Turkenburg, J.W. van Straten, W.H. de Wolf, and F. Bickelhaupt, J. Amer. Chem. Soc., 102, 3256 (1980).
3. A.D. Ketley, A.J. Berlin, E. Gorman and L.P. Fisher, J. Org. Chem., 31, 305 (1966); contrary to this procedure, one flow pyrolysis at 285°C was sufficient for a satisfactory conversion.
4. L. Skatteb$\o$l, J. Org. Chem., 29, 2951 (1964).
5. J.W. van Straten, J.J. van Norden, T.A.M. van Schaik, G. Th. Franke, W.H. de Wolf, and F. Bickelhaupt, Recl. Trav. Chim. Pays-Bas, 97, 105 (1978).
6. M. Makosza and M. Fedorynski, Synthetic Communications, 1973, 305.
7. H.G. Kuivila, Synthesis, 1970, 499.
8. ^{1}H NMR ($CDCl_3$, δ in ppm):

   3a (90 MHz): 4.37 (t of t, J = 8.5 and 2.5 Hz, 1 H, X part of A_2B_2X system); 3.75 (s, 1 H); 2.35 ($A_2B_2[X]$: δ_A = 2.63, δ_B = 2.09, J_{AB} = 15.5 Hz, J_{AX} = 8.5 Hz, J_{BX} = 2.5 Hz, 4 H); 2.1-1.2 (m, 10 H).

   3b (90 MHz): 4.35 (t of t, J = 9.2 and 10.3 Hz, 1 H, X part of A_2B_2X system); 3.35 (s, 1 H); 2.21 ($A_2B_2[X]$: δ_A = 2.30, δ_B = 2.11, J_{AB} = 14 Hz, J_{AX} = 9.2 Hz, J_{BX} = 10.3 Hz, 4 H); 2.1-1.2 (m, 10 H).

   9 (250 MHz): 5.82 (AB part of ABXY system, δ_A = 6.07, δ_B = 5.58, J_{AB} = 10.5 Hz, $J_{AX}\approx J_{AY}$ = ca 1 Hz, J_{BX} = J_{BY} = 8 Hz, 2 H); 3.61 (bs, 1 H); 3.56 (bs, 1 H); 2.63-2.24 (m, 3 H, including XY part of ABXY system at 5.82 ppm) 2.21-2.05 (m, including AB system with $\delta_A-\delta_B$ = 0.107, J_{AB} = 7 Hz, 3 H); 1.85-1.72 (m, 2 H); 1.56-1.42 (m, 2 H).

   10 (250 MHz): 6.40 (bs, 1 H); 5.90 (AB part of ABXY system, δ_A = 6.02, δ_B = 5.77, J_{AB} = 11.5 Hz, $J_{AX}\approx J_{AY}$ = ca 1 Hz, J_{BX} = 8.5 Hz, J_{BY} = 9.5 Hz, 2 H); 3.77 (bs, 1 H); 2.46 (m, 1 H); 2.36 (AB, $\delta_A-\delta_B$ = 0.024 ppm, J_{AB} = 7.5 Hz, 2 H); 2.0 (m, 4 H, including XY part of ABXY system at 5.90 ppm); 1.73 (m, 1 H); 1.32 (m, 2 H).
9. C.H. DePuy, Accts. Chem. Res., 1, 33 (1968).
10. L.A. Paquette, E. Chamot and A.R. Browne, J. Amer. Chem. Soc., 102, 637 (1980).
11. U. Burger, Chimia, 33, 147 (1979).
12. U. Burger and G. Gandillon, Tetrahedron Letters 1979, 4281.
13. G. Gandillon, B. Bianco, and U. Burger, Tetrahedron Letters 22, 51 (1981).

(Received in UK 19 June 1981)