α'β-ELIMINATION AND WITTIG REARRANGEMENT OF The carbanion from Benzyl Cyclooctyl Ether

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Summary. Beside the Wittig rearrangement and the migration of the cyclooctyl radical to the para position, the title carbanion gives rise to an elimination in a syn process.

Carbanions derived from ethers lead to the Wittig rearrangement which is in competition with an elimination reaction (1). The extent of this elimination varies considerably with the substrate (1c, 1g). The rearrangement likely occurs through dissociation to a radical pair (2, 3) which is compatible with the partial racemisation of the migrating group (2, 4, 5). In a recent CIDNP study of the carbanion derived from alkyl t betyl ether(6),it was shown that it is isobutene rather than the Wittig rearrangement product (2) which is polarized. Beside an early study (1g) on dibenzobicyclo 2,2,2 octadiene-2-0 benzyl which showed a predominant α ' β elimination in addition to trans E_2 and α elimination, the mechanistic pathway on the elimination product has received little attention. In a previous study on carbanions derived from thioethers (7), we showed that elimination was mainly syn with benzyl cyclooctyl thioether.

Mild synthesis of benzyl ethers derivatives (8) prompted us to study the benzyl cyclooctyl ether <u>1</u> derivative. The ether <u>1</u> was metalated at -78°C by n-BuLi in THF-HMPT 10-1 or by sec-BuLi in hexane or THF in the presence of tetramethylethylene-diamine (TMEDA). Cyclooctene (purely cis) and benzyl alcohol were formed in about 60 % yields. The products in THF-HMPT 10-1 at 0°C were : Wittig alcohol <u>3</u> (12 %), two aldehydes <u>4</u> and <u>5</u> (the corresponding aromatic aldehyde) (13 % together), glycol diether <u>6</u> (7.5 %) and cyclooctanol (3 %) (9). The aldehydes <u>4</u> and <u>5</u> result from the migration of the cyclooctyl group to the para position. Analogous aldehydes and ketones have been isolated in minor amounts during Wittig rearrangements



(4, 10-12). Compound <u>6</u> arises from the coupling of two α benzyl cyclooctyl ether radicals likely formed by electron transfer from the carbanion to HMPT. Temperature and medium changes had little effect on the composition of reaction products, in contrast with the results obtained from the carbanion derived from dibenzylthioether (13).

The stereochemistry of the elimination was studied with cis- β - 2 H₁ cyclooctyl benzyl ether <u>2</u> (2 H₀ 8.4 %, 2 H₁ 91 %, 2 H₂ 0.5 %) (14) which was prepared by deuteroboration (15) of cis cyclooctene and subsequent etherification under argon to avoid epimerisation (8, 16). Cis relationship and monodeuteration was ascertained by 2 H-NMR (Eu(fod)₃) on cis- β - 2 H₁ cyclo-octanol.

After metalation of ether 2 with n-Buli for 2 hrs in THF-HMPT 10-1 at -78°C, the solution was allowed to evolve 4 hrs at 0°C. The deuterium content determined by G.C. coupled to M.S. (17) was respectively ${}^{2}\text{H}_{0}$: 41 %, ${}^{2}\text{H}_{1}$: 59 % for cyclooctene and ${}^{2}\text{H}_{0}$: 67 %, ${}^{2}\text{H}_{1}$: 33 % for benzyl alcohol. This corresponds to a loss from the cyclooctyl group of 32 % of deuterium which was transferred to the benzyl alcohol. The location of the deuterium in the cis cyclooctene was found to be at the allylic position by ${}^{2}\text{H}-\text{NMR}$ (7, 18). So quite clearly, the elimination of the carbanion derived from benzyl cyclooctyl ether is a purely syn process and thus an α 'ß elimination. The primary isotope effect was found to be 1.8.



The $\alpha'\beta$ elimination could very well be a concerted process (a) or a radical process (b) when the dissociation is followed by a hydrogen transfer from the free radical to the radical anion. The results presented here seem to favour a concerted $\alpha'\beta$ elimination. However, the absence of temperature or solvent effects on the elimination: rearrangements ratio is surprising in view of a concerted mechanism for elimination and dissociative mechanism for rearrangements. A recent proposal that the |1,2| and |1,6| rearrangements of carbanion derived from an ether occurs from a set of non equilibrating radical pairs (11b) could explain the present results. The hydrogen transfer would follow the dissociation in a radical pair where the initial geometrical arrangement is still retained and thus would be a stereospecific process as observed in the present study. The stereoselectivity of this elimination likely depends on the nature of the group involved.

Notes and Bibliography

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- (9) ¹H NMR 250 MHz (CDC1₃) -
 - <u>3</u>: δ 1.2-2.0 ppm (15H); 4.40 (d, J=7 Hz, 1H); 7.3 (5H); MS M⁺ 218. The ketone obtained by chromic oxidation - NMR (CDCl₃): δ 1.65 (14H); 3.48 (m, 1H); 7.53 (m, 3H); 7.93 (m, 2H); MS M⁺ 216.
 - <u>4</u>: δ 1.2-2.0 ppm (14H) ; 2.96 (m, J=6.5 Hz, 3.3 Hz, 1.7 Hz, 2H) ; 3.18 (m, J=6.5 Hz, 3.5 Hz, 1H) ; 5.78 (AB, J=11 Hz, $\delta_A^{-}\delta_B^{-}$ 0.06 ppm) ; 6.87 (t, J=3.5 Hz, 1H) ; 9.42 (s, 1H).
 - 5 : δ 1.2-2.0 ppm (14H) ; 2.84 (m, 1H) ; 7.35 (d, J=2.3 Hz, 2H) ; 7.79 (J=8.3 Hz, 2H) ; 9.96 (1H).
 - <u>6</u>: δ 1.28 ppm (m, 10H); 1.5 (m, 4H); 3.12 and 3.37 (m, 1H); 4.24 and 4.42 (s, 1H); 7.1-7.4 (m, 5H).
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- (18) No trans-cyclooctene was detected and the deuterium labeling pattern shows that no isomarisation of trans to the cis-cyclooctene seemed to occur.

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