

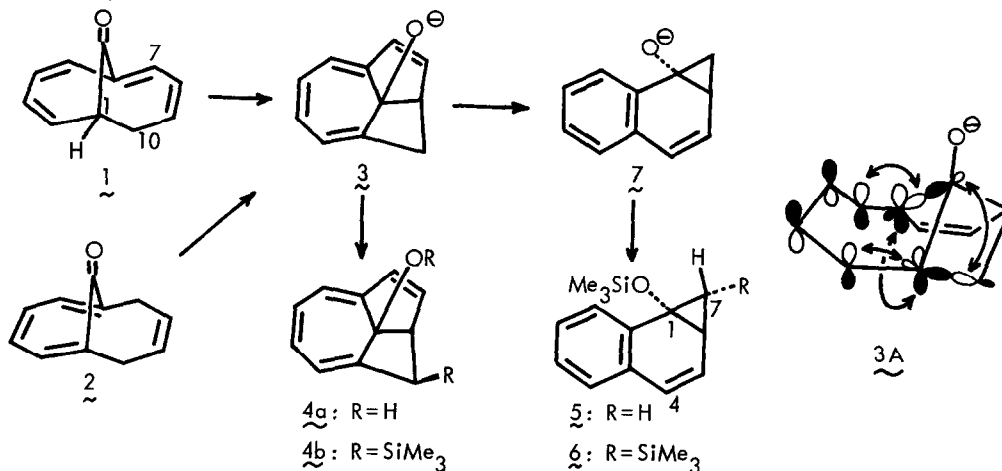
EFFECT OF TEMPERATURE AND COUNTER ION ON THE SKELETAL REARRANGEMENT
 OF A DIHYDRO[10]ANNULEN-11-ONE

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Abstract: Base-catalyzed rearrangement of bicyclo[4.4.1]undeca-2,4,6,8-tetraen-11-one under aprotic conditions revealed a novel anion-induced thermal process to a tricyclic cyclopropyl alcohol.

In our previous papers on the base-catalyzed reaction of bicyclo[4.4.1]undeca-2,4,6,8-tetraen-11-one (1), we have reported the formation of dehydro[4](2,7)troponophane (2) under protic conditions¹⁾ and of the tricyclic alkoxide 3 under aprotic conditions²⁾. By raising reaction temperature, however, we have found that 3 underwent a novel symmetry controlled skeletal rearrangement. The effect of alkali metal ion on the rearrangement has also been observed. The result is described herein.

The formation of the ion 3 (~93% yield) from 1 with LDA (3 eq) in THF at -78°C was established by the spectroscopic detection (in solution) of unstable 4a, the corresponding alcohol, and by the isolation of the silyl derivative 4b after trimethylsilylation²⁾. When the reaction mixture was brought to room temperature for 30 min. and then trapped by chlorotrimethylsilane (TMSCl), a complex mixture



of the products was obtained with no indication of the presence of either 2 or 4b. The only product isolated was the cyclopropanol derivative 5 (13% yield), colorless oil, whose structure was deduced from its spectra; m/e : 230 (M^+ , b), 215, 200, 185, 157, 141; $\lambda_{\max}^{\text{c-hex}}$: 221 (log ϵ 4.24), 237sh (4.12), 245 sh (3.92), 272 nm (3.93); ν^{oil} : 3025, 2950, 1480, 1455, 1417, 1341, 1245, 1217, 1070, 979, 920, 840, 778 cm^{-1} ; $\delta_{\text{H}}^{\text{CDCl}_3}$: 7.76 (1H, dd, $J=7.5, 1.8$), 7.35 (1H, ddd, $J=7.9, 7.5, 2.1$), 7.25 (1H, td, $J=7.9, 1.8$), 7.21 (1H, dd, $J=7.9, 2.1$), 6.33 (1H, dd, $J=8.0, 3.1$), 6.31 (1H, dd, $J=8.0, 3.1$), 2.19 (1H, ddt, $J=10.8, 5.6, 3.1$), 1.78 (1H, dd, $J=10.8, 4.8$), 0.03 (9H, s), -0.22 (1H, dd, $J=5.6, 4.8$); $\delta_{\text{C}}^{\text{CDCl}_3}$: 0.81 (q), 16.4 (dd), 27.0 (d), 57.5 (s), 123.6 (d), 125.7 (d), 125.9 (d), 126.7 (d), 127.2 (d), 128.0 (d), 129.3 (s), 136.9 (s). When KDA (2.5 eq) was used in place of LDA, 5 was obtained in 47% yield after 4 min. at -78°C , along with 2% of 4b. By raising the reaction temperature (-20°C , 4 min.), the yield of 5 improved to 77%³). That potassium ion is responsible for the increase of the yield was demonstrated also by the use of KOtBu (2.5 eq); the yield was 64% at -78°C and 77% at -20°C ⁴). These experiments clearly indicated 1) the intervention of two discrete anionic species 3 and 7 in the basic solution, 2) a thermal rearrangement of 3 to 7, and that 3) the rate enhancement of the reaction by softer K^+ compare with harder Li^+ , similar to the effect of metal ions in oxy-Cope and the related [3,3]sigmatropic rearrangements⁵). The same anion 7 formed also from 2 with KOtBu (2.5 eq) at -78°C after 5 min., and was trapped as 5 in 60% yield. However, the reaction of 1-7,10,10-d₃ with KOtBu (2.5 eq) at -20°C , yielded 5-d₃ in which all deuterium atoms were located at 4 and 7 positions, eliminating the intermediacy of 2 in the reaction 1→5. If the reaction involved 2 as an intermediate, the deuterium at 10 β position of 1 would have been lost in the product⁷).

The skeletal rearrangement 3→7 may be rationalized as a novel, thermally allowed, concerted 10 electron (HOMO-LUMO-LUMO three body interaction) process, orbital correlation of which can be depicted for example in 3A. The correlation is reminiscent of the vinylogous di- π -methane rearrangement⁶). The driving force for such a skeletal rearrangement would be the short distance of two 6π termini (2.385 Å for 3b²) and the strained σ -framework in 3, and the aromatization in the ion 7.

Thus, thermal reaction of an anion was shown to take a completely different course from that of neutral species of the same carbon skeleton.

References and Notes

- 1) Y. Fujise, T. Shiokawa, Y. Mazaki, Y. Fukazawa, M. Fujii and S. Itô, *Tetrahedron Letters*, **23**, 1601 (1982).
- 2) Y. Fujise, T. Morishima, K. Namiwa, T. Shiokawa, Y. Fukazawa and S. Itô, *ibid.*, **24**, 4261 (1983).
- 3) When a large excess (10 eq) of KDA was used (4 min., -20°C), bis-silylated product 6 was obtained (30%) together with 5 (8%) after trapping with TMSCl.
- 4) During work-up, which inevitably employs acid treatment or SiO_2 chromatography, 5 sometimes undergoes ring opening to a mixture of double bond isomers of benzo[b]cycloheptadienone.
- 5) S.R. Wilson and D.T. Mao, *Tetrahedron Letters*, 2559 (1977). D.A. Evans and D.J. Baillargeon, *ibid.*, 3319 (1978).
- 6) T. Sato and S. Itô, *ibid.*, 1051 (1979).
- 7) In the equilibrating conditions (KOtBu, tBuOD/THF, -78°C), 1 gave 2-d₁, which contains a deuterium at 7 β -position only.