

A Transannular Beckmann Rearrangement in Liquid Sulfur Dioxide

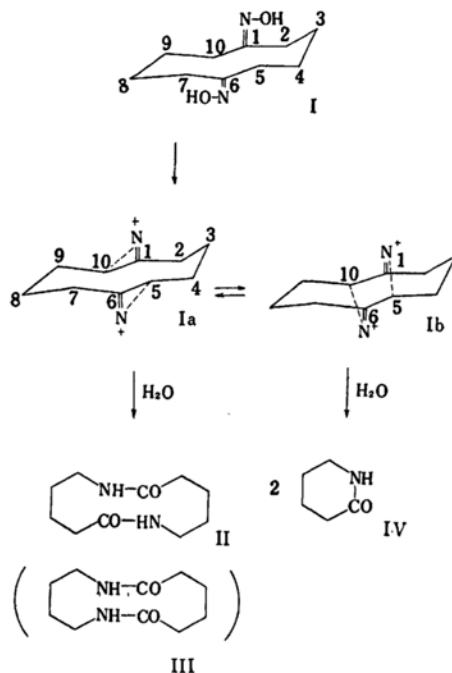
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In medium sized alicyclic compounds, transannular reactions have often been observed¹⁻³. This communication is concerned with an abnormal Beckmann rearrangement, the nature of which should be attributed to a novel transannular type of reaction.

When cyclodecane-1,6-dione dioxime (I) reacted with sulfur trioxide in liquid sulfur dioxide at room temperature for twelve hours, followed by elimination of sulfur dioxide by evaporation and addition of ice water to the reaction residue, a hitherto unreported cyclic oligomer of δ -valerolactam, 1,7-diaza-6,12-dioxocyclodecane (II) (yield 75%), separated out as fine crystals, m.p. (purified by sublimation) 264~266°C (Found: N, 13.9%. Calcd. for $C_{10}H_{18}O_2N_2$: N, 14.1%; mol. wt. Found: 215. Calcd. 198; ninhydrin test, negative⁴; I. R. ν_{max}^{KBr} : 1650 (CO), 3280 (NH) cm^{-1}). The I. R. spectrum of II closely resembles the spectra of cyclic oligomers of ϵ -caprolactam⁴. As we could find no diamine or dicarboxylic acid in the acid hydrolyzed product of II, absence of III (another possible product of rearrangement) in the reaction mixture was proved.

However, when the reaction was carried out with thionyl chloride in place of sulfur trioxide in liquid sulfur dioxide similarly as described above, followed by extraction with chloroform and evaporation of the solvent, I afforded a brown viscous nitrogen-containing liquid (27%), the structure of which was difficult to be identified. The residual solution after the extraction was made slightly alkaline with sodium hydroxide and again extracted with chloroform. The chloroform solution was condensed and the residue was subjected to distillation in vacuo. A yellow oil (IV) b.p. 90~93°C (2mmHg) was obtained. IV was identified as δ -valerolactam (33%),



$n_D^{20}=1.5339$ (Found: N, 13.8%. Calcd. for C_5H_9ON : N, 14.1%, N-(4-carboxyl butyl) phthalimide, m.p. and mixed m.p. with an authentic specimen, 117.5~118.5°C⁵). Its I. R. spectrum also coincided with that of IV described in the literature⁶. That δ -valerolactam (IV) was not a secondary product derived from II was demonstrated when II reacted in liquid sulfur dioxide with thionyl chloride at room temperature. No appreciable formation of IV was observed.

As the distances between the nitrogen atoms and carbon atoms (C_5 and C_{10}) are sufficiently close to permit an equilibrium state between the structures Ia and Ib, the latter being favored by thionyl chloride, the completion of the rearrangement, involving cleavage of C_1-C_{10} and C_5-C_6 linkages, gives rise to formation of IV. In such a case, a transannular Beckmann rearrangement is the most plausible explanation for the formation of IV from I in liquid sulfur dioxide.

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