

A BASE-INDUCED HOMOALLYLIC TYPE REARRANGEMENT IN A HOMOCUBANE SYSTEM¹⁾

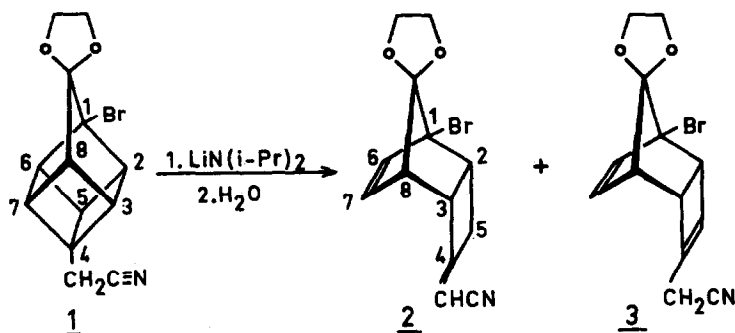
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(Received in UK 24 April 1972; accepted for publication 3 May 1972)

In the course of our study on strained bridgehead alcohols we recently reported the interesting stereospecific base-catalyzed homoketonization reaction of a homocubane bridgehead alcohol²⁾. This paper describes a carbon analog of this homoketonization e.g. a homoallylic type rearrangement.

Two possible substrates were considered for this process, namely the nitrile 1 and the carboxylate 2. Treatment of the cyanide 1³⁾ with lithium diisopropylamide in THF⁴⁾ at 0° resulted in an oil, in almost quantitative yield, consisting of a mixture of two alkenes to which the structures 2 and 3 were assigned on basis of spectral and chemical evidence (Scheme I). This cage-degradation reaction represents the first example of a homoallylic type⁵⁾ rearrangement in a strained cage system.

Scheme I



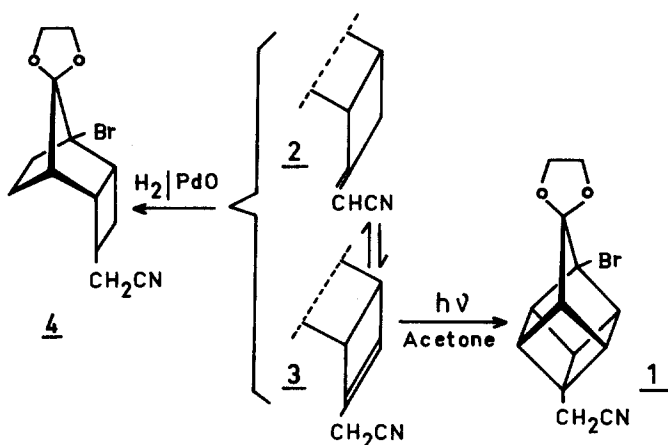
The IR spectrum of the mixture shows cyanide bands at 2220 and 2250 cm⁻¹, indicative of the presence of a conjugated and a non-conjugated -C≡N function. A weak olefinic absorption was observed at 3060 cm⁻¹. The NMR spectrum exhibits three olefinic signals i.e. a small multiplet at δ 6.02 ppm for H₅, H₆ and H₇ of 3, a doublet at δ 6.27 for H₆ and H₇ of 2 and a multiplet at δ 5.08 for the

proton adjacent to the cyanide group in 2. This olefinic part of the spectrum was unravelled by means of spin decoupling, INDOR and solvent shift experiments. The ethylene ketal function appears as an unsymmetrical multiplet at δ 3.75-4.35, while the remaining protons were found at δ 2.2-3.85 as a complex pattern.

The relationship between 2 and 3 became evident when the mixture was treated with lithium diisopropylamide in THF and subsequently quenched with H_2O . The ratio of 2 and 3 changed completely by an allylic rearrangement which interconverts 2 and 3. Several attempts were made to separate the olefines 2 and 3, (glc and tlc) but none of them was successful.

Hydrogenation of the mixture of 2 and 3 with H_2/PdO gave a single product 4, m.p.112-115 $^{\circ}$, in 95% yield (Scheme II).

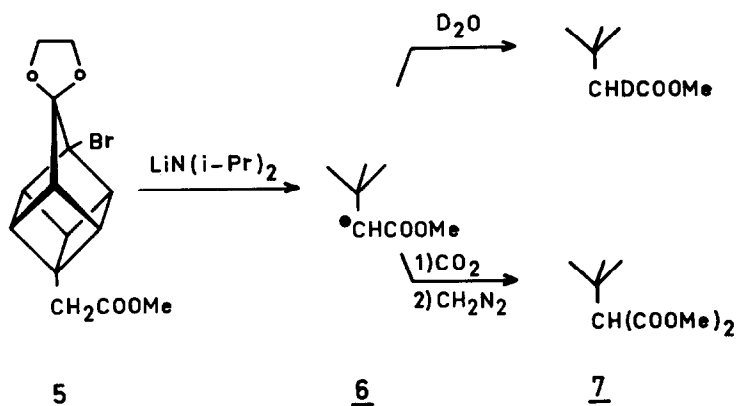
Scheme II



This compound $C_{13}H_{16}BrO_2N$ displays a $C\equiv N$ infrared absorption at 2245 cm^{-1} , NMR signals for the ethylene ketal group at δ 3.75-4.40 (symm.m., 4H) and the remaining proton signals between δ 1.6 and 3.2 ppm as a complex multiplet. Substantial support for the proposed structures in Scheme I was obtained from the irradiation of the mixture of the olefines in acetone. Because of the spatial arrangement of the double bonds in 3 photochemical cage closure may be expected, as indeed was found to be the case (Scheme II).

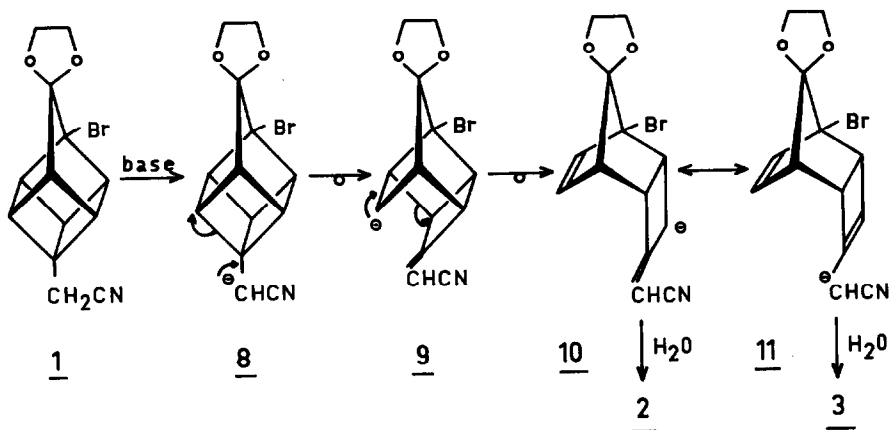
In a similar way the carboxylate⁶⁾ 2 was subjected to treatment with lithium diisopropylamide in THF. However, after work-up starting material was recovered almost quantitatively. Anion formation indeed had taken place since work-up with D_2O resulted in mono- and di-deuterated 2. Treatment of the anion 6 with CO_2 gave the malonic acid half ester which was converted into the diester 7 with CH_2N_2 in an overall yield of 76% (Scheme III). No cage degradation products were found at all.

Scheme III



In analogy with the homoketonization reaction²⁾, we propose a ring-opening mechanism for 1 as outlined in Scheme IV.

Scheme IV



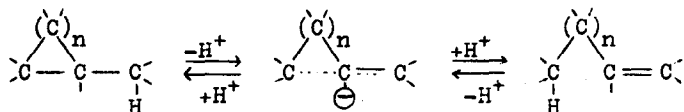
Under the applied aprotic conditions the rearrangement does not stop⁷⁾ at the stage of the half-cage carbanion 9, but another C-C-bond is broken by a second homoallylic rearrangement leading to the mesomeric carbanions 10 and 11. The double }-homoallylic rearrangement of 1 proceeds by an initial specific cleavage of the C₄-C₇ (or the identical C₄-C₃ bond). No products arising from the cleavage of the central C₄-C₅ bond were observed. Most likely the driving force in this homoallylic rearrangement is relief of ring strain. Cage constraint effects are probably also responsible for the initial specific cleavage

of the C_4-C_7 ($\equiv C_4-C_3$) bond.

The different behaviour of cyanide 1 and carboxylate 2 can be explained by the difference in stabilization of the intermediate α -carbanions. The carboxylate 2 is converted into a stable enolate anion⁴), minimizing the negative charge at the α -C atom and therefore preventing the homoallylic rearrangement. Presumably a considerable negative charge is required at the α -C atom to initiate this homoallylic type rearrangement in strained cage systems.

References

1. Chemistry of Strained Polycyclic Compounds. Part IV. Part III: A.J.H. Klunder and B. Zwanenburg, Tetrahedron, 28, (1972) in press.
2. A.J.H. Klunder and B. Zwanenburg, Tetrahedron Letters, 1971, 1721.
3. The cyanide 1 was prepared from the corresponding homocubane-4-carboxylic acid¹⁾ by a $LiAlH_4$ -reduction to the homocubane-4-methyl alcohol, conversion of the latter into the tosylate and subsequent substitution of the tosylate group by sodium cyanide in DMSO.
4. M.W. Rathke and A. Lindert, J.Amer.Chem.Soc. 93, 2318 (1971); S. Reiffers, H. Wijnberg and J. Strating, Tetrahedron Letters, 1971, 3001
5. A homoallylic rearrangement induced by base is defined by the following scheme (cf. the concept of homoketonization/homoenolization, A. Nickon and J.L. Lambert, J.Amer.Chem.Soc. 88, 1905 (1966):



The present study deals with a β -homoallylic rearrangement.

6. The carboxylate 2 was prepared from the corresponding homocubane-4-carboxylic acid¹⁾ by an Arndt-Eistert homologation.
7. Homoketonization of homocubane-4-alcohol under aprotic conditions also gave an entire degradation of the homocubane skeleton leading to a similar ring opening product as in the homoallylic type rearrangement of the cyanide 1. A.J.H. Klunder and B. Zwanenburg, to be published, See also ref.2.