

parentheses for the atoms in the asymmetric unit for complex I and II are listed in Table 1.

Table 1. Atomic coordinates.

I			
<i>x</i>	<i>y</i>	<i>z</i>	
Tl	0.0	0.2117(2)	0.0
Se	-0.2578(4)	0.0	0.0533(5)
S	0.0551(6)	0.0	0.2616(7)
P	-0.1441(8)	0.0	0.2521(9)
C ₁	-0.188(3)	0.157(4)	0.351(3)
C ₂	-0.135(4)	0.298(4)	0.317(4)

II			
<i>x</i>	<i>y</i>	<i>z</i>	
Tl	0.0	0.0858	0.25
S	0.1407(7)	-0.1251(5)	0.1219(12)
P	0.0	-0.2132(6)	0.25
C ₁	0.111(3)	-0.306(2)	0.386(4)
C ₂₁ ^a	0.216(7)	-0.375(5)	0.323(10)
C ₂₂ ^a	0.019(7)	-0.395(5)	0.461(12)

^a Methyl carbon positions in the disordered ethyl group.

Acknowledgement. The authors thank Dr. Wilhelm Kuchen, Institut für Anorganische Chemie der Universität Düsseldorf, for samples of crystals.

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Received May 23, 1973.

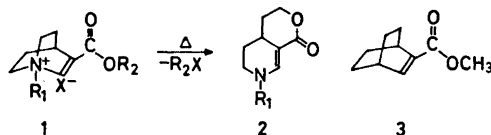
Bicyclic Enamines

VII. Attempted Thermal Rearrangement of 3-Methoxycarbonylbicyclo[2,2,2]oct-2-ene*

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Recently we reported that unsaturated quinuclidine-3-carboxylic acid esters^{1,2} were rearranged to lactones of type 2 when heated for a few seconds at about 150°. Similarly, we observed that amides corresponding to 1 under such conditions gave imino lactones.³ To study if similar



rearrangements also occurred in other bicyclic systems, we have now synthesized the bicyclo[2,2,2]oct-2-ene carboxylate 3 and heated this compound to 200° for 15 h. We found that 3 was stable under these conditions.

The rearrangement of 1 to 2 was originally interpreted as a sigmatropic rearrangement.² However, the thermal stability of 3 may indicate that other mechanisms are involved in the formation of the lactone 2, since sigmatropic rearrangements are likely to occur in both compounds 1 and 3.

Experimental. General comment. Melting points were determined with calibrated Anschütz thermometers in an electrically heated metal block. IR-spectra were recorded using a Perkin-Elmer 457 spectrophotometer and the NMR-spectra were measured with a Varian A 60 instrument using CDCl₃ solutions.

* Part VI of this series: Dolby, J., Hasselgren, K.-H., Castensson, S. and Nilsson, J. L. G. *Acta Chem. Scand.* **26** (1972) 2469.

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Chemical shifts are expressed in δ ppm relative to tetramethylsilane. Mass spectra were obtained using an AEI 30 instrument at 70 eV.

2-Cyano-2-hydroxybicyclo[2,2,2]octane. To a solution of bicyclo[2,2,2]octane-2-one⁴ (7 g; 56 mmol) in ether (30 ml) and saturated aqueous solution of potassium cyanide (3.9 g; 56 mmol), 1 N HCl solution (80 ml) was added dropwise with stirring at room temperature. The reaction mixture was then stirred for 60 min. The ether layer was separated, and the aqueous solution was extracted with ether (3 \times 20 ml). The combined ethereal solution was washed with water, dried (MgSO₄) and evaporated under reduced pressure. The white solid residue had m.p. 145–146° (from hexane), 8.3 g; 99% yield. ν_{\max} (KBr): 3250 cm⁻¹ (OH), 2225 cm⁻¹ (CN). (Found: C 71.4; H 8.4; N 9.2. Calc. for C₈H₁₃NO: C 71.4; H 8.4; N 9.2.)

2-Carbamoyl-2-hydroxybicyclo[2,2,2]octane. The above cyanohydrin (8.3 g; 55 mmol) was mixed with conc. HCl (100 ml) and kept for 17 h at room temperature. The white solid formed was filtered off and more product was obtained by ether extraction of the filtrate. The product (10 g; 75% yield) had m.p. 147–148° (from methanol). ν_{\max} (KBr): 3360 cm⁻¹ (OH), 3275 and 3195 cm⁻¹ (NH₂) and 1650 and 1600 cm⁻¹ (CO). Mass spectrum showed a molecular ion peak at m/e 169. (Found: C 63.4; H 9.1; N 8.3. Calc. for C₉H₁₅NO₂: C 63.9; H 8.9; N 8.3.)

2-Hydroxy-2-methoxycarbonylbicyclo[2,2,2]octane. A mixture of the above amide (10 g; 58 mmol), methanol (25 ml) and conc. HCl (10 ml) was refluxed for 4 h. The cooled reaction mixture was evaporated under vacuum and the residue (oil) was distilled to give a colorless liquid, b.p. 61–68°/0.05 mmHg. (9 g; 90% yield). ν_{\max} (film): 3400 cm⁻¹ (OH), 1715 cm⁻¹ (CO) and 1225 cm⁻¹ (–COC–). Mass spectrum showed a molecular ion peak at m/e 184. (Found: C 65.2; H 8.7. Calc. for C₁₀H₁₆O₃: C 65.2; H 8.8.)

2-Methoxycarbonyl-bicyclo[2,2,2]oct-2-ene. A solution of the above hydroxy ester (1 g; 6 mmol) in purified thionyl chloride (15 ml) was refluxed for 15 h. The excess thionyl chloride was evaporated under vacuum at room temperature and the oily residue was purified by thick layer chromatography (silica gel plates in light petroleum/ether; 9:1) which gave a colorless liquid (625 mg; 72% yield). ν_{\max} (film): 3020 (C=C–H), 1710 cm⁻¹ (C=O), 1615 (C=C), and 1220 cm⁻¹ (COC). Mass spectrum showed a molecular ion peak at m/e 166. (Found: C 72.0; H 8.5. Calc. for C₁₀H₁₄O₂: C 72.3; H 8.5.) NMR δ = 7.1 and 7.2 (d, together 1H, C=C–H, $J \sim 2$ cps)

3.63 ppm (s, 3H, O–CH₃), and 1.15–1.64 ppm (m, 10 H, aliphatic protons).

Heating of 3-methoxycarbonyl-bicyclo[2,2,2]oct-2-ene. The unsaturated ester 3 was heated without solvent, in a sealed tube (under N₂ gas), at 200° (oil bath) for 15 h. Samples were taken out periodically and checked by TLC, IR, and NMR. The compound showed a thermal stability under these conditions.

Acknowledgement. A fellowship to M. M. Al Holly from the International Seminar in Physic and Chemistry at Uppsala University is greatly acknowledged. This work has also been supported by the *Swedish Natural Science Research Council*.

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Received June 15, 1973.

Correction to "Mass Spectrometry of Onium Compounds. Part XIII."*

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In the structural formulas for compounds XIV a,b–XVII a,b R⁵ and R⁸ must be interchanged.

Received May 21, 1973.

* *Acta Chem. Scand.* **26** (1972) 3459.