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The Synthesis of Bicyclic Lactam Ether

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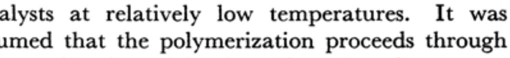
The bicyclic lactam ether, 3-aza-10-oxabicyclic[4.3.1]decane-4-one has been attempted to synthesize by the Beckmann rearrangement of the oxime of 9-oxabicyclo[3.3.1]nonane-3-one; this rearrangement caused polymerization through the cleavage of the ether group in acidic media. Therefore, it may be presumed that the cationic polymerization of lactam ethers in the presence of Lewis acid proceeds through the opening of the ether linkage.

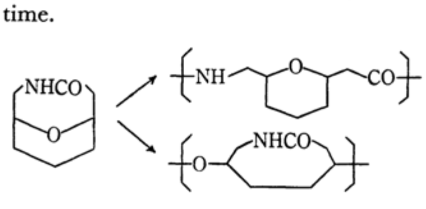
The polymerization of lactam ethers gave[1] polyamide ethers in the presence of Lewis acid catalysts at relatively low temperatures. It was assumed that the polymerization proceeds through the coordination of Lewis acid to the ether group, followed by the cleavage at the ether group, since lactams do not polymerize under the same reaction conditions. However, lactam ethers give the same kind of polyamide ethers by means of the cleavage of either ether or amide linkages, and the reaction scheme is not clear.



$$\left[\begin{matrix}\text{NHCO}\\ \text{O}\end{matrix}\right] \rightarrow \left[-CH_2CH_2CONHCH_2CH_2O-\right]$$

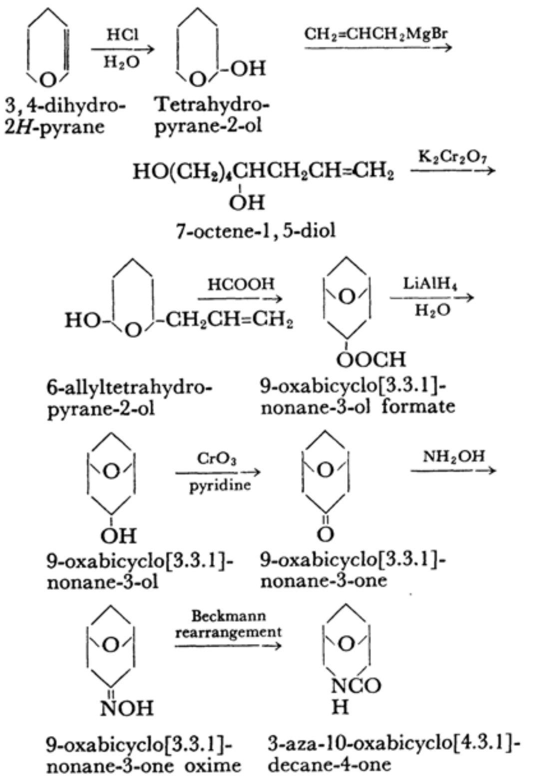
The ring-opening polymerization of the following bicyclic lactam ether gives different kinds of polymers according to whether the ring-cleavage occurs at the amide or ether linkages: hence, the structural analysis of the resultant polymer should show where the ring-opening occurs.

Therefore, the synthesis of 3-aza-10-oxabicyclo-[4.3.1]decane-4-one has been attempted for the first time.



Experimental

The synthetic route of 3-aza-10-oxabicyclo[4. 3. 1]-decane-4-one is shown as follows:



Tetrahydropyrane-2-ol.—A solution of 94 g. of purified dihydropyrane in 400 ml. of 0.2 N hydrochloric acid was heated under reflux for 1 hr. After the solution had been neutralyzed by sodium hydroxide, the product was extracted with ether and distilled. B. p. 60.7—65.0°C/9 mmHg; yield, 88.3 g. (74%).

Found: C, 58.65 (58.80); H, 9.83% (9.87).

7-Octene-1, 5-diol.—A solution of 61 g. (0.5 mol.) of allylbromide in 200 ml. of ether was dropped, with stirring, into 300 ml. of ether in the presence of 72 g.

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[1] N. Ogata, T. Asahara and S. Tohoyama, *J. Polymer Sci.*, to be published.

(3.2 mol.) of magnesium. The mixture was heated for a period of 4 hr. at such a rate that the ether refluxed gently; then the solution was heated at a gentle reflux for an additional 30 min. The Grignard solution was transferred into a 1 l. three-necked flask, and then a solution of 15 g. of tetrahydropyrane-2-ol in 150 ml. of ether was added, drop by drop. The solution was heated under reflux for an additional 40 min. and then decomposed with a saturated aqueous solution of ammonium chloride. The product was extracted with ether and distilled. B. p. 114—127°C/5 mmHg; yield, 11.4 g. (53%).

Found: C, 66.42 (66.43): H, 11.18 (11.24); mol. wt., 148 (144).

6-Allyltetrahydropyrane-2-ol.—A portion of 15 g. (0.1 mol.) of 7-octene-1, 5-diol was dissolved in 30 ml. of benzene, and then 65 ml. of a Beckmann solution (12 g. $K_2Cr_2O_7$, 10 g. H_2SO_4 and 120 ml. of water) was

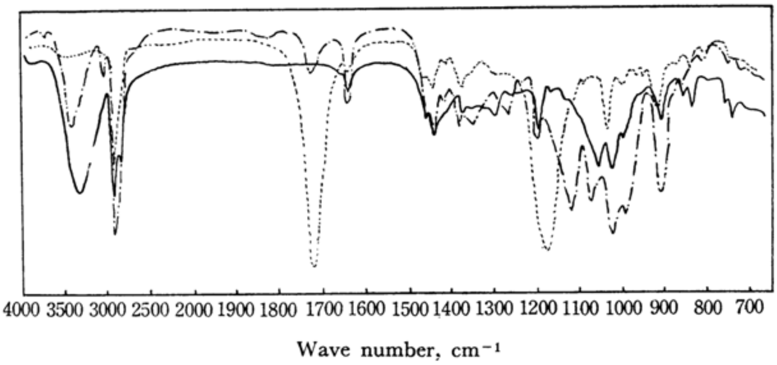

Fig. 1. Infrared spectra of products (KBr)
----- 6-Allyltetrahydropyrane-2-one
------ 9-Oxabicyclo[3.3.1]nonane-3-ol formate
——— 9-Oxabicyclo[3.3.1]nonane-3-ol

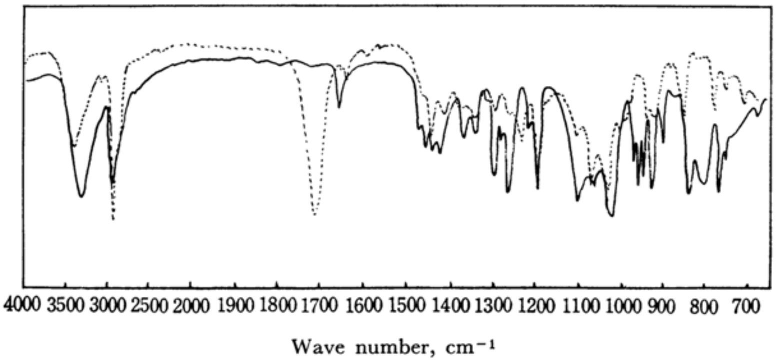

Fig. 2. Infrared spectra of products.
---- 9-Oxabicyclo[3.3.1]nonane-3-one
—— 9-Oxabicyclo[3.3.1]nonane-3-one oxime

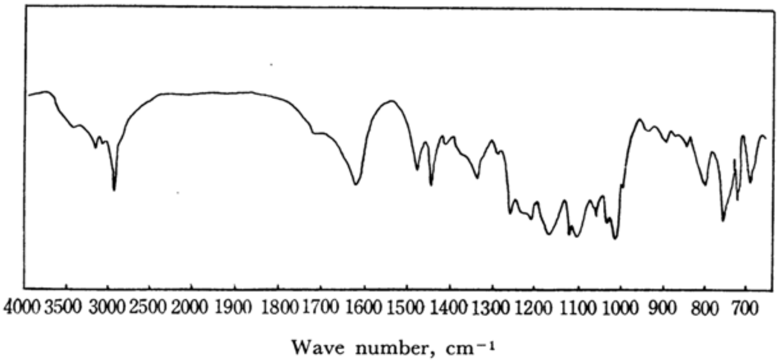

Fig. 3. Infrared spectrum of polymer (Film).

dropped, with stirring, into the solution over a period of 2 hr., with the temperature maintained at 35°C. The stirring was then continued for an additional hour at 35°C. The benzene layer was separated, and the aqueous solution was extracted twice with 100 ml. of dichloroethane. Benzene and dichloroethane solutions were combined, washed with water, and dried in the presence of magnesium sulphate. The distillation of the solution gave a fraction (7.2 g. (48%)) of 120—128°C/0.5 mmHg. The infrared spectrum of the product is shown in Fig. 1.

Found: C, 66.57 (66.77); H, 9.93% (9.78).

9-Oxabicyclio[3. 3. 1]nonane-3-ol formate. — A solution of 7.45 g. (0.05 mol.) of 6-allyltetrahydropyrane-2-ol in 50 ml. of 92% formic acid was heated while being stirred for 1 hr. at 40°C and then distilled. The gaschromatographic analysis of the distillate showed two peaks in almost equivalent amounts; separation could not be effected either by distillation or by column chromatography. The analytical data as well as the infrared spectrum showed that the distillate was the aimed-for product and it might include stereoisomers. B. p. 96—102°C/3 mmHg; yield, 4.83 g.

Found: C, 62.97 (63.51); H, 8.25 (8.29); mol. wt., 170 (170).

9-Oxabicyclo[3. 3. 1]nonane-3-ol.—A solution of 4.8 g. of 9-oxabicyclo[3. 3. 1]nonane-3-ol formate in 50 ml. of ether was added, drop by drop, into a solution of 4.8 g. of lithium aluminum hydride in 200 ml. of ether, with the temperature maintained at 0°C. The solution was allowed to stand, while being stirred for an additional 2 hr. at 0°C, then it was decomposed with a saturated aqueous solution of ammonium chloride. A continuous extraction with ether, followed by distillation, yielded 8 g. (80%) of the product. B. p. 132—134°C/0.5 mmHg.

Found: C, 66.90 (67.6); H, 9.00 (9.20).

9-Oxabicyclo[3. 3. 1]nonane-3-one.—A solution of 1.5 g. (0.01 mol.) of 9-oxabicyclo[3. 3. 1]nonane-3-one in 20 ml. of pyridine was added, drop by drop, into a solution of 4.2 g. (0.042 mol.) of chromic acid in 42 ml. of pyridine, with the reaction temperature at 0°C. kept by the use of an ice bath. Stirring was then concontinued at room temperature for an additional 4 hr., after which the solution was neutralized by the addition of concentrated hydrochloric acid. Continuous extraction, followed by the removal of the ether, yielded 0.78 g. of the product.

Oximation. — 9-Oxabicyclo[3. 3. 1]nonane-3-one (2 g.(0.014 mol.)), hydroxylamine hydrochloride (2 g.) and sodium carbonate (2 g.) were dissolved in a mixture of 20 ml. of ethanol and ether; the solution was then heated under reflux for 20 hr. After the solution had been extracted with ether and the ether removed, white crystals were obtained. The recrystallization of these from ethanol yielded 1.2 g. (56%) of needle crystals, m. p. 124—125°C.

Found: C, 60.40 (61.9); H, 8.30 (8.4); N, 8.5% (9.0) mol. wt., 160 (155).

Beckmann Rearrangement.—A strong reagent for the Beckmann rearrangement, such as sulfuric acid, decomposed oximes with an ether group, and mild reaction conditions, using thionyl chloride at a low temperature, have been recommended[1] for the synthesis of lactam ethers.

In this case, however, not even thionyl chloride could give the aimed-for product; only a sticky polymer was obtained. Neither phosphorus pentachloride nor benzene sulfonyl chloride could give the aimed-for bicyclic lactam ether, even at such a low temperature as below 0°C., and the product was a polymer with molecular weight of about 580 to 650. The polymer was a soft solid, and its melting point was not clear. The infrared spectrum of the polymer is shown in Fig. 3.

Found: C, 61.5 (61.9); H, 8.5 (8.4); N, 8.6% (9.0).

Discussion

Bohlmann[2] synthesized 9-oxabicyclo[3.3.1]-nonane-3-ol through the alkaline hydrolysis of the formate of the alcohol. However, the yield was poor by this method; the reduction of the formate, followed by hydrolysis, gave a better yield of the alcohol. The oxidation of the alcohol into ketone in the presence of the chromic acid-pyridine complex gave a better yield than in the Beckmann solution ($K_2Cr_2O_7/H_2SO_4$) since a ring cleavage was observed in an acidic medium. Pure bicyclic lactam ether was not able to isolate by means of the Beckmann rearrangement of the oxime, but a polymer was easily obtained. The infrared spectrum of the polymer showed absorption resulting from the amide group at 3250, 3100 and 1625 cm^{-1}. The strong absorption at 1625 cm^{-1} is supposed to be due to an amide carbony group; no absorption was observed in the range from 1550 to 1600 cm^{-1}.

The chain trans amide group shows a strong absorption, the so-called amide II band, in the region from 1550 to 1600 cm^{-1}. Therefore, the ring cleavage may be presumed to have occured at the ether linkage, because no absorption resulting from a chain trans amide group was observed, as would be expected if the amide group was cleaved.

The derivatives of bicyclic ether show an absorption band resulting from the ether group in the region from 1030 to 1020 cm^{-1}, while the cleaved product of the bicyclic lactam ether shows an ether band at 1010 cm^{-1}. A monocyclic oxime ether, tetrahydro-γ-pyrone oxime and its isoxime, gave an absorption band resulting from the ether group at 1100 cm^{-1}, a band which was shifted to 1070 cm^{-1} in the polymer from a monocyclic lactam ether, tetrahydro-1, 4-oxazepine-5(4*H*)-one. The tetrahydropyrane derivatives show an ether band around 1100 cm^{-1}. Therefore, the shift of the ether band toward a lower frequency also support the above presumption.

The protonation of the ether group, followed by the cleavage, caused the polymerization of bicyclic lactam ether at a low temperature. Therefore, the cationic polymerization of lactam ethers proceeds

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[2] F. Bohlmann, H. T. Schulz and J. Poamann, *Tetrahedron Letters*, **1964**, 1705.

through the opening of the ether group. Further evidence on the structure of the polymer will provide for the elucidation of the reaction scheme.

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