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## The Dehydration of Triterpenoid Ring A $\epsilon$ -Lactams

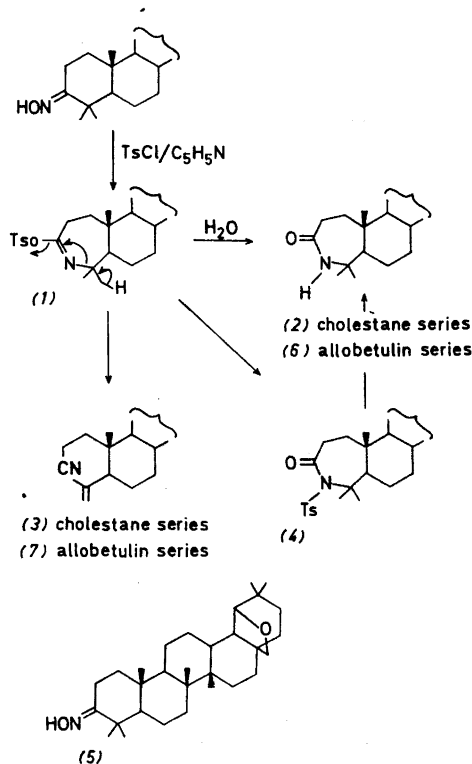
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In a recent communication<sup>1</sup> the mechanism of the "abnormal" Beckmann rearrangement<sup>2</sup> of triterpenoid oximes was discussed. In that particular case a mixture of the  $\epsilon$ -lactam (2) and the seconitrile (3) was obtained by the treatment of 4,4-dimethyl-5 $\alpha$ -cholestan-3-one oxime with tosyl chloride in pyridine. It was proposed that the reactions involve the initial formation of the tosyloxy-imine (1) in agreement with the generally accepted mechanism of the "normal" Beckman rearrangement.<sup>3</sup> (1) on hydrolysis gives the  $\epsilon$ -lactam (2) either directly<sup>1</sup> or via the *N*-tosyl lactam (4),<sup>3</sup> or eliminates tosic acid in the manner indicated to give (3). (1) and (4) must be interconvertible since prolonged reaction times favour the (presumably irreversible) formation of (3) at the expense of (2).

The failure of isolated (2) to provide (3) under the same conditions was considered further to support the mechanism given.<sup>1</sup> However, it is probable that this observation has no bearing on the mechanism as it merely indicates that (2) is not tosylated under the conditions. The use of more forcing conditions in the tosylation of (2) to give (1) or (4)\* should result in the formation of (3) if the mechanism of the seconitrile formation is correct.

The treatment of *allobetulone* oxime (5),\*\* m.p. 262°C (decomp.), with tosyl



chloride in pyridine gave, after one week at room temperature, 37% of the  $\epsilon$ -lactam (6), m.p. 322°C, and 48% of the seconitrile (7), m.p. 256°C, with no starting material or *allobetulone* being recovered. Two days at room temperature gave 81% of (6) whereas two days at 90°C gave 59% of (7) and no (6) from (5). The  $\epsilon$ -lactam (6) yielded, after 11 days at room temperature, in the presence of tosyl chloride in pyridine, only starting material, whereas (6) was converted to (7) in three days in 36% yield by the same reagent at 90°C.

Similarly, the  $\epsilon$ -lactam obtained by the Beckmann rearrangement of methyl 18 $\beta$ -H-3-oxoglycyrrhetate oxime is reported<sup>5</sup> to yield 50% of the corresponding seconitrile on heating in pyridine in the presence of tosyl chloride.

The results are in agreement with the mechanism given<sup>1</sup> and clarify the role of the  $\epsilon$ -lactam.

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\* Dehydration of prim. amides by tosyl chloride in pyridine to give nitriles<sup>4</sup> is thought to involve *O*-tosylation.

\*\* All new compounds have been characterized by the usual spectroscopic methods and satisfactory elemental analysis.

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## The Synthesis of 2-Amino-3-cyano Derivatives of 4,5-Dihydrofuran and 5,6-Dihydro-4H-pyran, and their Transformation to Lactones

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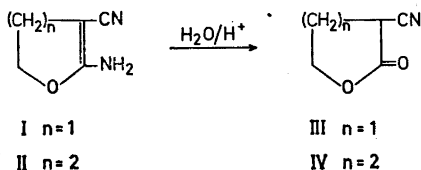
Recently, the synthesis of some substituted 2-amino-3-cyano-4,5-dihydrofurans from the sodium derivative of malonitrile and substituted ethylene oxides was reported.<sup>1</sup> This prompts the following report of a convenient preparation of 2-amino-3-cyano-4,5-dihydrofuran (I) and 2-amino-3-cyano-5,6-dihydro-4H-pyran (II) from the sodium salt of malonitrile with

tendency for base catalysed cyclisation exists for  $\gamma$ - and  $\delta$ -hydroxynitriles with activating  $\alpha$ -substituents to give the stable enamine form of this type of iminolactones. The reported conversion of  $\alpha$ -cyanolactones to 3-carbethoxy derivatives of 2-amino-dihydro-furans and pyrans<sup>3</sup> seems to be an expression of the same tendency. These facts, and the ease with which the enamines are hydrolysed to carbonyl compounds, make this route to  $\alpha$ -cyanolactones an attractive one. Particularly in the case of  $\delta$ -lactones the method is useful, since  $\alpha$ -cyano- $\delta$ -lactones are not otherwise easily obtainable.  $\alpha$ -Cyano- $\gamma$ -lactones, on the other hand, are conveniently prepared from cyanoacetic ester with ethylene oxides.<sup>4-6</sup>

In the hydroxyalkylation of the sodium salt of malonitrile, 3-bromopropanol was much more reactive than 2-bromoethanol. The same phenomenon is observed in the reaction of these compounds with  $\alpha$ -carb-ethoxy lactones,<sup>2</sup> and the low reactivity of 2-bromoethanol in malonic ester synthesis has been reported earlier.<sup>7</sup>

That the cyclic compounds (I) and (II) are present in the enamine and not in the imino form, can be seen from their strong ultraviolet absorption at about 225 m $\mu$ .<sup>8</sup> The low infrared stretching frequency of the cyano group at 2175 cm<sup>-1</sup>, and the presence of three and four NMR absorptions of equal intensities for the compounds (I) and (II), respectively, can only be explained by the enamine structure.

Acid hydrolysis rapidly transformed the dihydrofuran (I) and the dihydropyran (II) derivatives to the  $\alpha$ -cyano- $\gamma$ - (III) and  $\delta$ - (IV) lactones, respectively.



2-bromoethanol and 3-bromopropanol, respectively. The dihydropyran derivative was of particular interest as an intermediate in the synthesis of  $\alpha$ -cyano- $\delta$ -valerolactone (IV), a compound needed in an investigation of C-H acidity of lactones, and as a possible precursor in the synthesis of  $\alpha$ -substituted  $\delta$ -lactones.<sup>2</sup> A pronounced

*Experimental.* 2-Amino-3-cyano-4,5-dihydrofuran (I). To finely divided sodium (7.8 g) in toluene (200 ml) and diethyl ether (200 ml) was added malonitrile (22 g) in ether (200 ml). The reaction mixture was heated to 50°, and dry ethanol (25 ml) added in small portions under stirring. When all the sodium was dissolved, 2-bromoethanol (42 g) was added dropwise, and the stirring continued for 12 h at 50°. After cooling, the reaction mixture was filtered, the solid matter washed with ether, and the solutions combined. The solvents were evaporated under reduced pressure, giving a yellowish, crystalline residue, which on recrystallisation from benzene gave almost colourless crystals (3.6 g, 10%), m.p. 113–114°. (Found: C 54.76; H 5.52; N 25.20. Calc. for C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O: C 54.54; H 5.49; N 25.49.) IR absorption bands (CHCl<sub>3</sub>) were found at 3450, 3350, 2175, 1640, and 1580 cm<sup>-1</sup>. NMR (DMSO-*d*<sub>6</sub>) shifts were observed at

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