SYNTHESIS OF NEW SULTAMS

A THESIS

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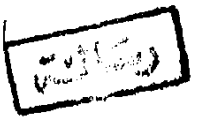

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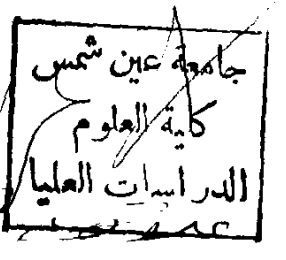

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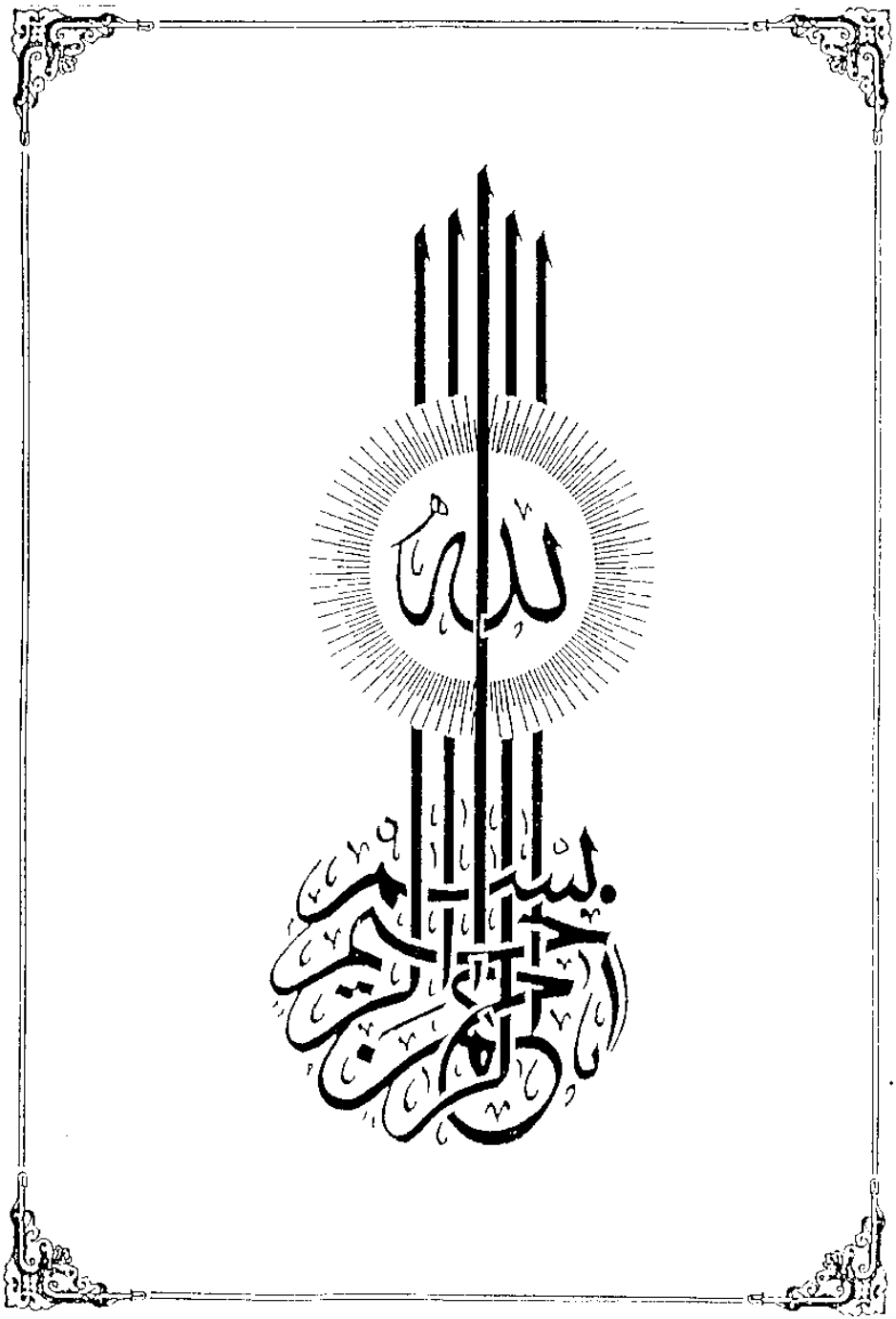

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ARABIC SUMMARY

SUMMARY

SUMMARY

The synthesis of N-substituted aminosulphonic acids by the reaction of propanesultone-(1,3)(XXXV) with amino-compounds, is described. The sulphonic acids (XXXVI-XXXIX) are prepared through the reaction between propanesultone-(1,3) and m-anisidine, 2,5-xylidine, 4-amino-3-nitro-toluine, p-chloro,p-bromo,p-iodoaniline, 1,8-diaminonaphthalene and 3,5-dichloro-1,4-phenylenediamine, respectively. (XXXV) reacts similarly with aliphatic amino-compounds, namely n-tetradecylamine, 2-amino-5-diethylaminopentane to give the sulphonic acids (XL) and (XLI), respectively. Heterocylic amino-compounds, exemplified by 3-amino-5-methyl-isoxazole, 2-amino-5-mercapto-1,3,4-thiadiazole and 4-amino-antipyrene react similarly with (XXXV) yielding the corresponding sulphonic acids (XLII-XLIV), respectively. The sulphonic acids (XXXVI-XLIV) are water soulble and exhibit remarkable acidity towards Na_2CO_3.

The sultams (La,b), (LI), (LII,a,b,c) and (LIII) were prepared by cyclization of the corresponding sulphonic acids (XLIX a,b), (XL), (XXXVII a,b,c) and (XXXVIc),respectively with boiling $POCl_3$. In order to prepare unsaturated sultams, 2,4-dimethyl-1,3-butadienesultones-(1,4) (LIV) is allowed to react with primary amines to give the corresponding N-substituted-3,5-dimethyl-1,3-butadienesultam-(1,4).

Thus, (LIV) reacts with 1,8-diaminonaphthalene, 2,5-dichloro-1,4-phenylenediamine, 2-ethylaniline and 2-amino-4-methyl-1,3-pyrimidine yielding the corresponding sultams (LVI-LIX), respectively.

Phenyldrazine reacts with (XXXV) to give the sulphonic acid (LX). This reaction of (XXXV) with acid hydrazides has been also investigated. Thus, when the sultone (XXXV) is allowed to react with phenylacetic acid hydrazide, benzoic acid hydrazide, p-anisic acid hydrazide, p-chlorobenzoic acid hydrazide, o-,m-,p-toluic acid hydrazides and salicylic acid hydrazide to give rise to the corresponding N-substituted hydrazino propane-1-sulphonic acids (LXI-LXIII), respectively. The sulphonic acids (LXI a,c) and (LXIII) are very hygroscopic, so they were seperated in the form of potassium salts.

In an attempt to carry out the reaction between acid hydrazide and 2,4-dimethyl-1,3-butadienesultone (1,4)(LIV), the nature of the product depends on the reaction conditions. If the reaction is carried out by fusion or in non-polar solvent, the corresponding sultam is obtained. When the reaction is carried out in polar solvents, such as alcohols the reaction tackes place in a different manner so that either the corresponding amino sulphonic acid (LXV) or the hydrazino derivative (LXVI) is obtained..Thus, (LIV) reacts with o-toluic acid hydrazide, p-toluic acid hydrazide, p-anisic acid hydrazide, p-nitrobenzoic acid hydrazide, p-chlorobenzoic acid hydrazide, phenylacetic acid hydrazide and

3-hydroxy-2-naphthoic acid hydrazide by fusion or in boiling xylene to give the corresponding sultams (LXVII-LXIX), respectively. (LIV) reacts with phenylacetic acid hydrazide, p-tolic acid hydrazide, isonicotinic acid hydrazide and p-nitrobenzoic acid hydrazide in boiling ethanol yielding the corresponding acids (LXX-LXXIII), respectively. (LIV) reacts in boiling n-butanol with o-toluic acid hydrazide, m-toluic acid hydrazide, salicylic acid hydrazide, p-anisic acid hydrazide and p-nitrobenzoic acid hydrazide to give rise to 4N-hydrazino-2,4-dimethyl-1,3-butadiene-1-sulphonic acid (LXVI) together with the butyl ester of the corresponding acid.

The previous work described the reaction of sultones with primary amines to yield either the sulphonic acid or the corresponding sultams. It has been found also that propanesultone-(1,3) reacts with secondary and tertiary amines yielding the corresponding inner salts of the type $\geq \overset{+}{N}-(CH_2)_3-\overset{-}{SO_3}$. Thus, (XXXV) reacts with triethylamine, diethylamino-ethanol, triethanol amine, N-methylpiperidine, 2-methylpyridine, 3-methylpyridine, caffeine, papaverine and ephiderine in boiling acetone to give the inner salts (LXXIV-LXXXII), respectively.

Bromination of some N-substituted propanesultam-(1,3) is studied to locate the position at which the bromine atom attacks the sultam molecule. Propanesultone-(1,3) reacts

with o-,m-,p-toluidine, o-,p-anisidine, o-,m- and p-aminobenzoic acid yielding the amino sulphonic acids (LXXXV a-h), respectively. The sultams (LXXXVI a-f) were obtained by cyclization of the corresponding sulphonic acids (LXXXV) by boiling with $POCl_3$. Bromine reacts with (LXXXVI a,b,c,f) yielding the monobromosultams (LXXXVII a-d), respectively.

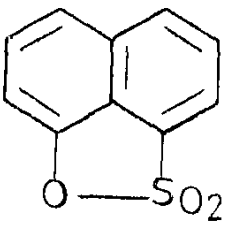
The structure of the produced compounds was confirmed, beside analytical data, by infared and ^{1}H-n.m.r. spectroscopy. The molluscicidal activity of some selected compounds have been tested and pronounced activity has been found.

INTRODUCTION

SULTONES AND SULTAMS

Sultones are the internal esters of hydroxysulphonic acids, correspond to lactones, and are generally five or six-membered rings, with or without olefinic bonds.

Sultams are the nitrogen analogues of sultones, stem from gamma, delta and epsilon-aminosulphonic acids. The first sultone prepared was 1,8-naphthosultone (I). This compound was analysed in 1887 by Schultz[1]. The compound was studied by Erdmann[2] who confirmed the structure and coined the term sultone.



(I)

Since the sultones are relatively more reactive than sultams, they serve as useful materials for the synthesis of detergents [3], dyestuff intermediates[4] and furan derivatives[5].

Methods of preparation

I. Preparation of sultones

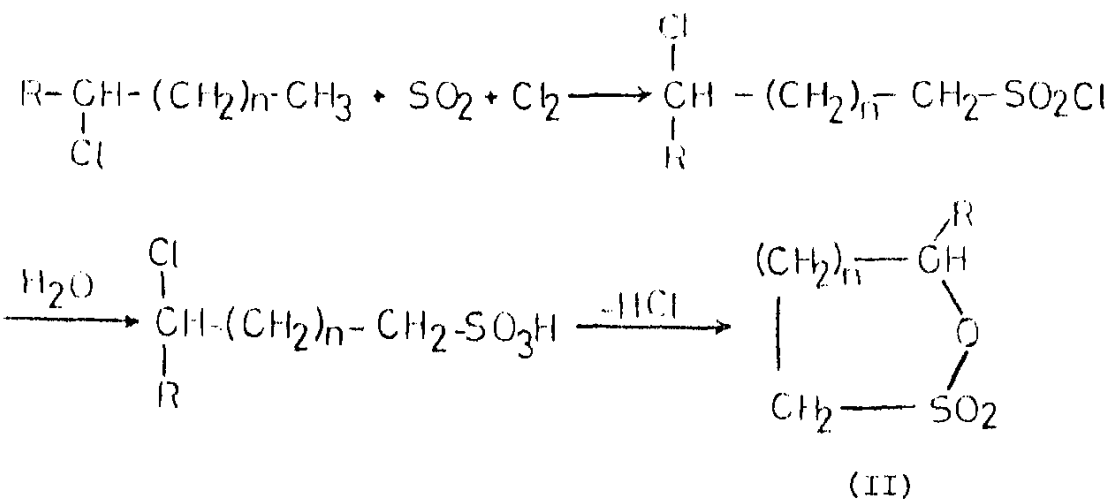
The general method for the preparation of sultones consists in the elimination of the elements of water

from the corresponding hydroxysulphonic acids, either by the action of heat or a mixture of concentrated sulphuric acid and acetic anhydride or by boiling the diazotized solution of an o- or peri- amino-arylsulphonic acid.

The synthetic methods of sultones can be classified as follows :

a) From alkylhalides

This method consists in irradiation of the appropriate alkyl halide, usually the chloride, in an atmosphere of sulphur dioxide and chlorine gas[6]. The sulphonyl chloride function of the resulting chlorosulphonyl chloride is hydrolyzed and the reaction mixture then heated to 90°C to give the sultone (II)[6,7].



(II)

While 1-chlorobutane gives a mixture of γ- and δ-butanesultones (III) and (IV) in addition to a mixture of dichlorobutanes. The higher chloroalkanes react similarly[7].

(III) (IV)

b) <u>From olefins</u>

from the corresponding hydroxysulphonic acids, either by the action of heat or a mixture of concentrated sulphuric acid and acetic anhydride or by boiling the diazotized solution of an o- or peri- amino-arylsulphonic acid.

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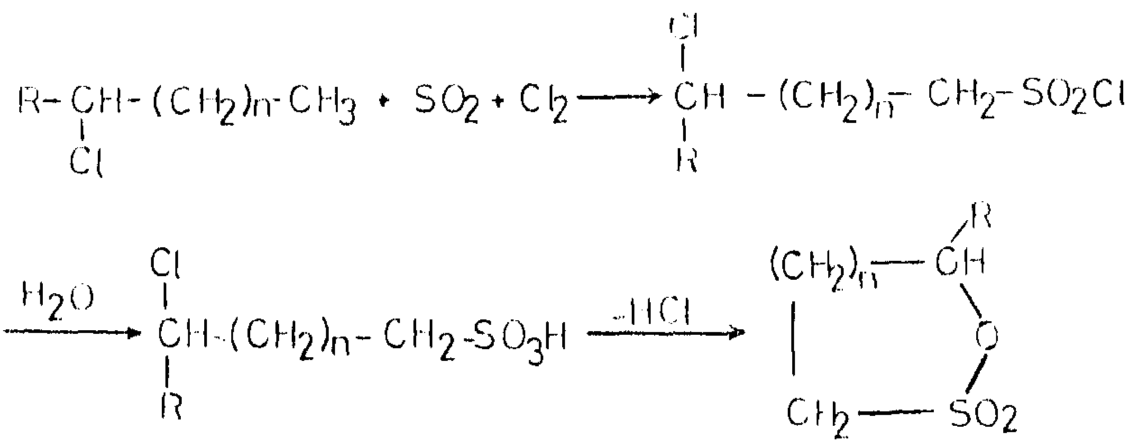

(II)