ENHANCED RATES OF HYDROLYSIS OF ESTERS BY AZACROWN ETHER DERIVATIVES

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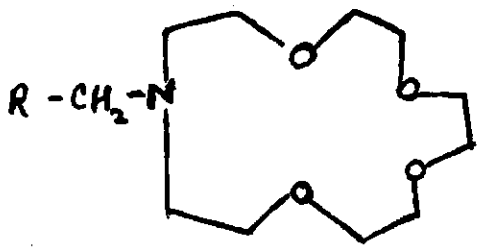
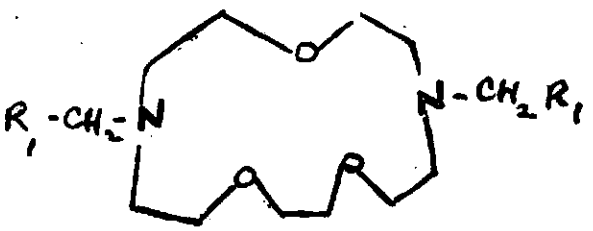
Several groups of workers are engaged in the synthesis of efficient and selective molecular catalyst to mimic enzymes(1). Rate enhancement in chemical reactions by substrate binding has been observed with cyclodextrins(2) hydrophobic systems(3) and crown ethers and their derivatives(4).

In this paper we report our results on the effect of azacrown ethers (I and II) having a hydroxy and amino groups on the ester hydrolysis reaction.



I (a) R = 2-Phenylethyl
(b) R = 2-(m-Hydroxyphenyl) ethyl



II (a) R_1 = 2-Phenylethyl
(b) R_1 = 2-(*O*-Hydroxyphenylethyl)
(c) R_1 = 2-(m-Hydroxyphenylethyl)
(d) R_1 = -CO-OMe

III $Br^-H_3\overset{+}{N}-CH_2-CO-C_6H_4-NO_2$

IV $Br^-H_3\overset{+}{N}-CH_2-CH_2-CO-O-C_6H_4-NO_2$

V $Br^-H_3\overset{+}{N}-CH_2-CO-NH-CH_2-CO-O-C_6H_4-NO_2$

(R) R_1 = -CO-NH-CH$_2$-CH$_2$-

The observed rate constants and relative rates for the hydrolysis of the esters III, IV and V catalysed by crownethers I and II are given in the Table below.

	Substrate	Catalyst	kx10^5 mol^{-1}ls^{-1}	Krcl (approx.)
1	III	I(a)	3.19	1
2.	III	I(a)+ *m*-cresol	3.31	1.05
3.	III	I(b)	141.4	44
4.	III	I(b)+ $MeNH_3Br^-$	31.5	10
5.	III	II(a)	2.88	1
6.	III	II(a)+ *m*-cresol	5.95	2
7.	III	II(b)	17.3	6
8.	III	II(c)	198	69
9.	III	II(c)+ $MeNH_3Br^-$	25.7	9
10.	III	II(d)	5.89	2

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	Sub-strate	Catalyst	kx10^5 mol^{-1} ls^{-1}	Krcl (approx)
11.	III	II(e)	31.9	11
12.	IV	I(a)	17.5	1
13.	IV	I(b)	66	3.9
14.	IV	II(q)	30.8	1
15.	IV	II(b)	38	1.2
16.	IV	II(c)	93.9	3.1
17.	V	I(a)	39	1
18.	V	I(a)+*m*-cresol	40.2	1
19.	V	I(b)	312	8
20.	V	I(b)+$MeNH_3Br^+$	82.5	2.1
21.	V	II(a)	30.1	1
22.	V	II(a)+*m*-cresol	29.5	1
23.	V	II(b)	61.6	2
24.	V	II(c)	270	9
25.	V	II(c)+$MeNH_3Br^+$	81.0	2.7
26.	V	II(d)	4.4	11
27.	V	II(e)	96.3	22

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SYNTHESIS OF SOME MONOAZA AND DIAZA-15-CROWN-5-COMPOUNDS

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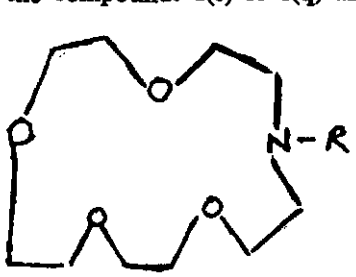
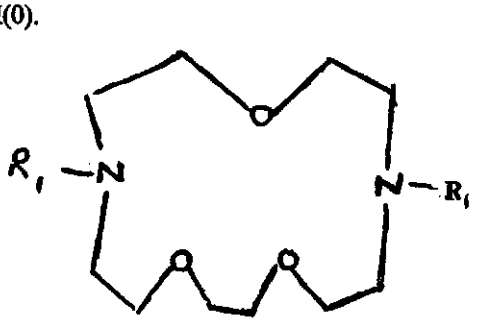
As a part of our investigations(2) in the chemistry of crown ethers(3) we studied the catalytic activity of suitably substituted aza crown ethers in the hydrolysis of p-nitrophenylesters of amino acids and peptides. For this study several monoaza and diaza-15-crown-5 compounds were synthesised and this paper discusses the synthesis of the compounds I(c) to I(q) and II(b) to II(0).



I



II

(a) R = Tosyl
(b) R = Hydrogen
(c) R = Benzyl
(d) R = 3-(*O*-Acetyloxyphenyl) propionyl
(e) R = 3-(*O*-Hydroxyphenyl) propionyl
(f) R = 3-(*O*-Hydroxyphenyl) propyl
(g) R = 3-Phenylpropionyl
(h) R = 3-Phenylpropyl
(i) R = *O*-Nitrocinnamoyl
(j) R = 3-(*O*-Aminophenyl) propionyl
(k) R = 3-(*O*-Aminophenyl) propyl
(l) R = M-Nitrobenzyl
(m) R = m-Aminobenzyl
(n) R = m-Nitrocinnamoyl
(o) R = 3-(m-Aminophenyl) propionyl
(p) R = 3-(m-Aminophenyl) propyl
(q) R = 3-(m-Ethylaminophenyl) propyl

(a) R_1 = Hydrogen
(b) R_1 = 3-(*O*-acetyloxyphenyl) propionyl
(c) R_1 = 3-(*O*-Hydroxyphenyl) propyl
(d) R_1 = 3-(m-Acetyloxyphenyl) propionyl
(e) R_1 = 3-(m-Hydroxyphenyl) propionyl
(f) R_1 = 3-(m-Hydroxyphenyl) propyl
(g) R_1 = 3-Phenylpropionyl
(h) R_1 = 3-Phenylpropyl
(i) R_1 = *m*-Nitrocinnamoyl
(j) R_1 = 3-(*m*-Aminophenyl) propionyl
(k) R_1 = 3-(*m*-Aminophenyl)propyl
((l) R_1 = Benzoyloxycarbonylmethyl
(m) R_1 = Methoxycarbonylmethyl
(n) R_1 = Carboxymethyl
(o) R_1 = Histaminocarboxylmethyl

Compounds I(a), I(b) and II(a) were synthesised by known[1] methods. Compounds I(c) to I(q) are synthesised from I(b) by either alkylation or acylation followed where necessary by reduction. Compounds II(b)–II(o) were synthesised by analogous methods from II(a). All new compounds are characterised by UV, IR, NMR spectroscopy and by high resolution mass spectral measurements.

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