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LETTERS TO THE EDITOR

SYNTHESIS OF THE FIRST DIBENZO(PERHYDROTRIAZINO)-AZA-14-CROWN-4 ETHERS

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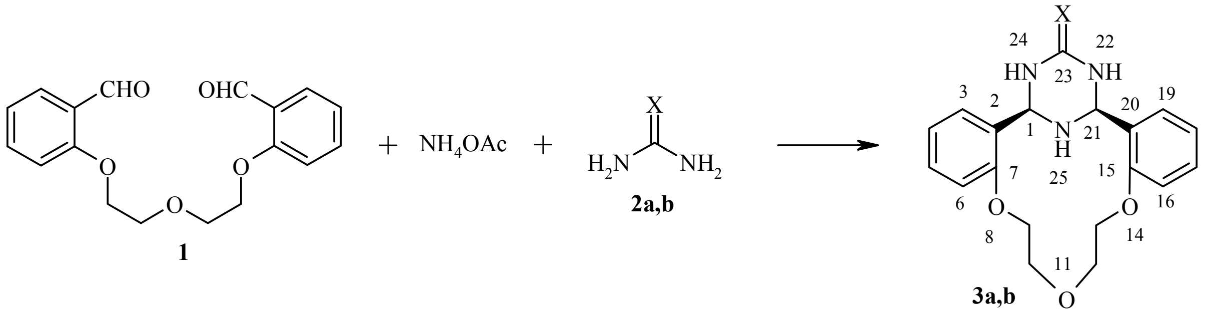
We have recently reported [1, 2] successful attempts to broaden the scope of the use of the Petrenko-Kritchenko reaction by introducing 1,5-bis(2-formylphenoxy)-3-oxapentane (**1**) in condensation with dialkyl ketones and ammonia. As a result single stage methods were developed for the synthesis of novel groups of azacrown ethers which contained a piperidone fragment having 2,6-diaryl substituents mutually bound with a polyethyleneoxide bridge [3, 4].

In this work we have studied the possible preparation of aza crown ethers whose macrocyle included a perhydrotriazine subunit in place of the piperidine fragment. With this in mind a three component condensation was carried out in alcohol and acetic acid solution (13 h, 20ºC) with urea, thiourea, and guanidine in place of the dialkyl ketones. In the case of urea chromato mass spectrometric data showed the formation of a complex mixture of linear condensation products.



2, **3** **a** X = S, **b** X = NH

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By contrast, change to thiourea **2a** or guanidine **2b** gave the crystalline perhydrotriazinoaza-14-crown-4 ether products **3a,b** in 73 and 28% yields respectively. The presence of seven heteroatoms in the two heterocycles within this novel heterocyclic system is attractive for studying the interaction of the fragments on the chemical properties of each and, overall, on the formation and stability of compounds coordinated with metal ions.

The ^{1}H NMR spectra were recorded on a Bruker WP-400 spectrometer (400 MHz) using DMSO-d_6 and with the residual proton signal of the deuterated solvent as internal standard. IR Spectra were taken on an IR-75 spectrometer for KBr tablets. The analysis of reaction mixtures and the purity of the compounds prepared was performed using Finnigan MAT 95 XL (EI, ionization energy 70 eV) and PE SCIEX API 165 (150) (Shimadzu HPLC SCL 10Avp, Gilson 215 autosampler, EASD Sedex 75, H^+ ionization ions) chromato mass spectrometers.

Azacrown Ethers 3a,b. A solution of dialdehyde **1** (3.14 g, 10 mmol), thiourea or guanidine (10 mmol), and ammonium acetate (1.0 g, 13 mmol) in a mixture of alcohol (30 ml) and acetic acid (2 ml) was stirred at 20ºC for 13 h. The precipitated crystals were filtered off, washed with ethanol, and recrystallized from chloroform to give compounds **3a,b**.

8,11,14-Trioxa-22,24,25-triazatetracyclo[19.3.1.0^{2,7}.0^{15,20}]pentacosa-2,4,6,15(20),16,18-hexaene-23-thione (3a). Yield 2.70 g (73%); mp 188-190ºC. IR spectrum, ν, cm^{-1}: 3397, 3322 and 3195 (NH), 1059 (C=S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.88-4.16 (3H, 4H, and 2H, respectively, three m, $OCH_2CH_2OCH_2CH_2O$, NH-25); 5.28 (2H, d, *J* = 11.6, H-1,21); 6.90 (2H, t, *J* = 7.6, H-4,18); 6.94 (2H, d, *J* = 8.0, H-6,16); 7.25 (2H, d, *J* = 7.6, H-3,19); 7.31 (2H, t, *J* = 8.0, H-5,17); 7.94 (2H, br. s, H-22,24). Mass spectrum, *m/z* (I_{rel}, %): 371 $[M]^+$ (26), 338 (38) $[M-SH]^+$, 326 (7), 311 (98), 297 (34), 296 (63), 251 (46), 192 (28), 148 (52), 146 (91), 121 (68), 122 (100), 121 (52), 119 (50), 107 (26), 91 (53), 78 (29), 77 (76), 76 (89). In ionization mode $[M+1]^+$ 372. Found, %: C 61.71; H 5.85; N 11.22. $C_{19}H_{21}N_3O_3S$. Calculated, %: C 61.44; H 5.70; N 11.31. M 371.

The structure of **3a** was proved unambiguously from X-ray analytical data as a complex with one molecule of chloroform and will be published separately.

23-Imino-8,11,14-trioxa-22,24,25-triazatetracyclo[19.3.1.0^{2,7}.0^{15,2}0]pentacosa-2,4,6,15(20),16,18-hexaene (3b). Yield 1.0 g (28%); mp 220-221ºC. IR spectrum, ν, cm^{-1}: 3307, 3252 (NH), 3653, 1616 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (3H, m, H-1,21,25); 3.25, 3.28, 4.10, and 4.21 (2H, 1H, 4H, and 1H respectively, all br. s, $OCH_2CH_2OCH_2CH_2O$); 6.81-7.46 (10H, m, H arom, H-22,24); 8.58 (1H, br. s, =NH at C(23)). Mass spectrum, *m/z*: 355 $[M+1]^+$ (ionization regime). Found, %: C 64.30; H 6.08; N 15.70. $C_{19}H_{22}N_4O_3$. Calculated, %: C 64.39; H 6.26; N 15.81. M 354.

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