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N-(HYDROXYALKYL)PYRROLES :
PRECURSORS FOR THE SYNTHESIS OF POLYPYRROLES BEARING ACTIVE CENTRES

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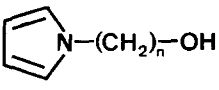
Abstract : N-(Hydroxyalkyl)pyrroles have been synthesized in good yields from halo-hydroxyalkanes and pyrrolyl potassium salt in DMSO-THF. These are compounds easy to handle and become precursors of specifically substituted pyrroles and polypyrroles.

The conducting polymer polypyrrole is a convenient material to elaborate polymeric modified electrodes containing a specific active centre [1,2]. Recently, [3] we have used a new way where the active centre is bound to the pyrrole nitrogen via an alkyl chain. In order to possess a fast and general procedure available for a large number of substituents, it is of interest to synthesize an easy to handle precursor.

We have initially directly synthesized N-bromo and N-chloroalkyl pyrroles in order to substitute the halogen by the specific active centre. However, usually, such compounds are difficult to purify, volatile and, as it has been previously reported, unstable [4].

Consequently, we turn to other classical reactive functions such as alcohol, and now report the synthesis of the following N-(hydroxyalkyl) pyrroles that appear as convenient starting materials.

1a n = 2
1b n = 3
1c n = 6
1d n = 11



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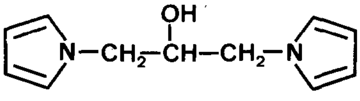

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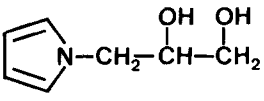

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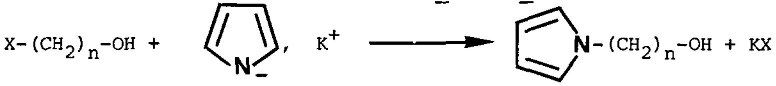
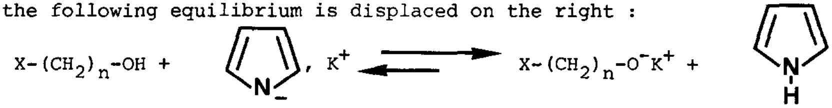
The choice in the synthesis of the 1-(ω-hydroxyalkyl)pyrroles series 1 has been directed by the interest of studying the influence of the aliphatic chain length on steric, redox or other interactions between the future active centre (replacing the hydroxyl group) and the pyrrole monomer or polymer. In compounds 2 and 3 , the precedent aspect remains, but here is added the variation of the ratio between polymerizability (pyrrolic groups) and reactivity (active centres).

To our knowledge, only 1a and 1b were known. They have been prepared either by condensation of the corresponding hydroxyalkylamine with 2,5-dimethoxytetrahydrofuran [5] in 70 % and 46 % yields, or by the BLICKE and BLAKE [6] method in 23 % and 22 % yields. 1a has been also synthesized by condensation of ethanolamine with 1,4-bis-(dimethylamino)-1,3-butadiene in 38 % yield.

We have synthesized compounds 1 a,b,c,d, 2 and 3, by action of the pyrrolyl potassium salt on the corresponding commercially available halo-hydroxyalkanes with improved yields in the case of the known products 1a and 1b.

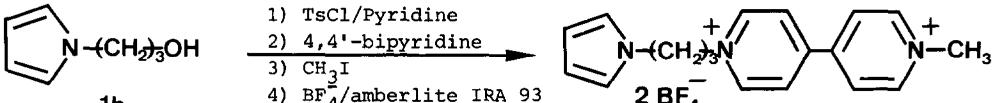


The pyrrole pK_a of 17.5 indicates that pyrrole is a weaker acid than many alcohols[7] and the following equilibrium is displaced on the right :



Consequently, to insure the stoechiometry in pyrrolyl potassium salt, we use it in a two-fold excess for the synthesis of compounds 1a,b,c,d. For compounds 2 and 3, three moles of pyrrolyl potassium salt are used for one mole of respectively 1,3-dichloro-2-propanol and 3-bromo-1,2-propanediol. The following experimental procedure has been pursued under argon in a dry box. Pyrrolyl potassium salt [8] (10^{-1} or 1.5×10^{-1} mol) is dissolved in 20 cm^3 DMSO then 50 cm^3 THF are added. A solution of the adequate bromo- or chloro-hydroxyalkane (5 x 10^{-2} mol) in about 20 cm^3 THF is slowly added to permit heat elimination. After ten minutes stirring, the solution is poured into 500 cm^3 water saturated with Na_2SO_4 and extracted several times with 100 cm^3 diethyl ether. The solvents and pyrrole present in the organic phase are eliminated under vacuum in a 80°C water bath. Chromatography of the crude oil on silica gel using diethyl ether as eluent provides the pure N-hydroxyalkyl pyrroles [9]. 1 a,b,c,d, 2 and 3 are obtained respectively in 71 %, 53 % 78 %, 93 %, 68 % and 48 % yield.

These alcohols react as usual with pyridines (via the tosylate) or aryl or sulfonyl chloride derivatives providing the corresponding N-alkyl pyrrole derivatives. These N-substituted pyrroles are easily electropolymerized allowing the synthesis of derivatized electrodes [1b,10]. For instance, starting from 1b, we prepare the 1-methyl-1'-(3-pyrrol-1-yl-propyl)-4,4'-bipyridinium tetrafluoroborate salt 4 (40 % yield)



1b

4

which, after electropolymerization, provides polymer films exhibiting redox and electrochromic properties [1b].

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References and notes :

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2. By specific active centres, we mean chemical groups exhibiting redox, electrochromic, photosensitive properties, such as metallic porphyrin viologen, ruthenium complex, etc...
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7. G. Yagil, Tetrahedron, **23**, 2855 (1967).
8. Pyrrolyl potassium salt is prepared in the dry box by action of potassium on pyrrole (5 % in excess) in THF. The white precipitate is filtered and dried under vacuum.
9. All compounds had correct chemical analysis (elemental or high resolution mass spectroscopy). IR spectra (neat) of these compounds are similar, and differ only by the ratio of the intensity of bands (cm^{-1}): 3400 (OH), 3100 (pyrrolic H), 2930-2940 (alkyl CH and CH_2). ^{1}H-NMR ($CDCl_3$) data follows : 1a, δ 3.21 (s, 1H), 3.42 (d, J = 6 Hz, 2H), 3.57 (d, J = 4.5 Hz, 2H), 6.03 (t, J = 2.2 Hz, 2H), 6.5 (t, J = 2.2 Hz, 2H) ; 1b δ 1.81 (q, J = 6 Hz, 2H), 3.07 (s, 1H), 3.42 (t, J = 6 Hz, 2H), 3.87 (t, J = 6 Hz, 2H), 6.07 (t, J = 2.2 Hz, 2H), 6.57 (t, J = 2.2 Hz, 2H) ; 1c δ 1.35-1.7 (br, 8H), 2.6 (s, 1H), 3.48 (t, J = 6 Hz, 2H), 3.78 (t, J = 6 Hz, 2H), 6.07 (t, J = 2.2 Hz, 2H), 6.57 (t, J = 2.2 Hz, 2H) ; 1d, δ 1.22 (s-br, 18H), 2.76 (s, 1H), 3.44 (t, J = 6 Hz, 2H), 3.7 (t, J = 6 Hz, 2H), 5.99 (t, J = 2.2 Hz, 2H), 6.48 (t, J = 2.2 Hz, 2H) ; 2 δ 2.28 (s, 1H), 3.65 (br, 5H), 6.07 (t, J = 2.2 Hz, 4H), 6.52 (t, J = 2.2 Hz, 4H) ; 3 δ 3.38-3.8 (br, 7H), 6.12 (t, J = 2.2 Hz, 2H), 6.62 (t, J = 2.2 Hz, 2H).
10. M. Salmon and G. Bidan, J. Electrochem. Soc., to be submitted.

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