Synthesis of pyrrole derivatives of serinol for functionalization of carbon allotropes

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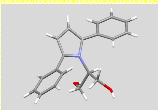
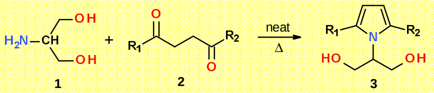
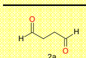
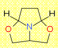
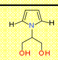
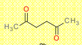
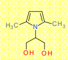
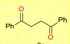
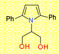
Summary: *N*-Pyrrole-based heterocycles are present in many natural products,[1] medicinal agents,[2] and functional materials,[3,4] therefore substantial attention has been paid to develop efficient methods for pyrroles synthesis.[5,6] Moreover, they are precursors for the synthesis of poly *N*-alkyl pyrroles which have wide ranging applications in electronics and sensors due to their tunable optoelectronic properties.

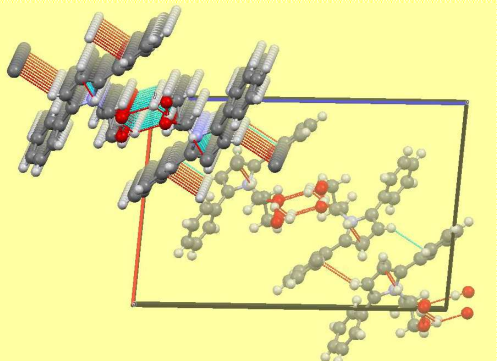
We present here one operationally simple, practical and economical Paal-Knorr pyrrole condensation of serinol (2-amino-propan-1,3-diol, **1**) with dicarbonyl compounds **2** (and related precursors acetal/ketals or enolesters), under neat conditions in the absence of any catalysts, which allows the synthesis of *N*-serinolpyrrole derivatives **3** in good to excellent yield.

N-serinolpyrroles **3a,b** were obtained in two steps from dicarbonyl compounds **2a** and **2b** through oxazolidine intermediates. The first step occurs at room temperature while in the second step oxazolidines are converted into pyrroles by heating. Pyrrole **3c** was obtained in one step by heating compound **2c**. In all cases solvents and catalysts were not used and yields were all good to excellent.

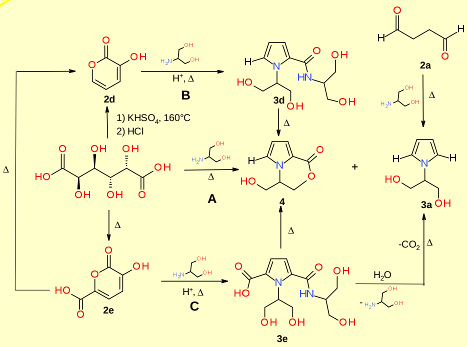




Reactant	T (°C)	t (h,')	Yield (%)	H	T (°C)	t (h,')	P	Yield (%)
 2a	25	6	98		90	4	 3a	98
 2b	25	6	98		130	7	 3b	85
 2c	-	-	-	-	130	6	 3c	90



Structure of 2,5-diphenyl *N*-serinol pyrrole **3c** from X-ray. Highlighted is the hydrogen bond of 4 oxygen network which divides the high polar and unpolar framework.

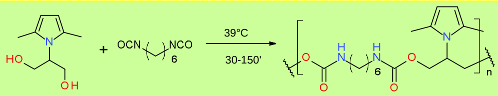


Scheme: Pathways to serinolpyrrol derivatives from mucic acid and its di-insaturated lactones.

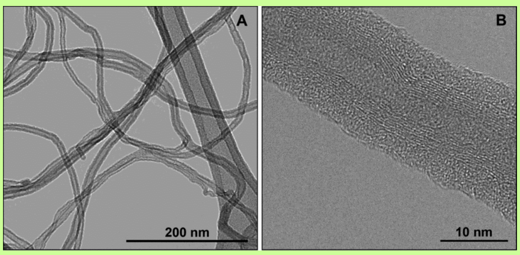
Mucic acid (as all aldaric acid) has an interesting thermal reactivity: on heating this compound loses water forming the corresponding unsaturated lactone **2e** which on further warming can be converted by decarboxylation into the 3-hydroxy-2-pyrone (**2d**). Pyrones **2e** and **2d** can undergo a nucleophilic attack by amines on lactone carbonyl group opening the ring to the corresponding substituted 1,4-diketons.

This reactivity was used to synthesize pyrroles **3a**, **3d**, **and 3e** by a mild and green process (50-70°C) using serinol (**1**) as nucleophilic agent (pathways **B** and **C**).

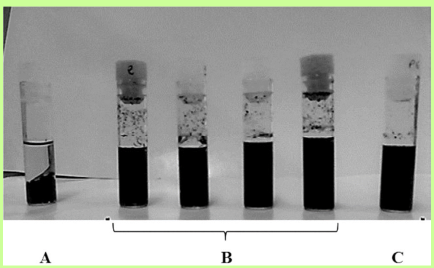
The pyrroles **4** and **3a** can be obtained conveniently also heating a mixture of mucic acid and serinol at 160°C for 3 hours (pathway **A**).



Polyurethanes (PU) were synthesized from 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propandiol (**3b**-SP) and hexamethylen-diisocyanate (HDI). Stable supramolecular interaction with multiwalled carbon nanotubes (MWCNT) was established.



HRTEM micrographs of: (A) individual tubes,(B) the MWCNT-PU adduct



Dispersions of MWCNT in acetone: (A) without additive; (B) with PU (four different polymer grade) after 12 months storage, (C) with PU after centrifugation (third vials from left to right of B).

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