PS11.09.04 REGIOSELECTIVE SYNTHESIS OF 2-(1H)PIRIDONES.

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Piridones are relevant in the pharmacological industry and the studies of their syntetic procedures is of interest, particularly those leading to regioselectivity.

In order to understand the mechanism of the regioselective synthesis of 2-(1H)piridones several products were isolated and characterised by NMR spectroscopy. Since the NMR experiments were not conclusive about the structures, X-Ray diffraction studies were carried out on the following compounds: $C_{14}H_{22}N_2O_3$, $C_{13}H_{19}N_3O$, $C_{17}H_{22}N_2SO_3$ (type B), $C_{11}H_9N_4O$, $C_{15}H_9N_4O$ (type C).
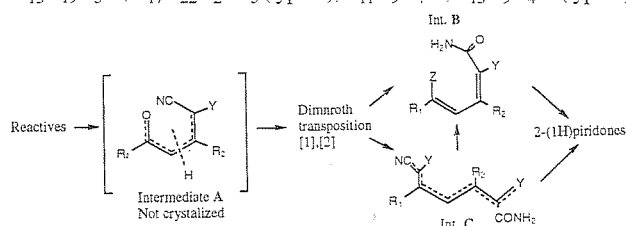
(Z=-Pyrrolidine; Y=-CN,CO_2Et,-$SO_2C_6H_5$; R_1=Me,Et,^{i}Pr,Ph,...; R_2=H,Me,^{i}Pr,Ph,...)

Solid state X-Ray studies provide explanations to most of the NMR questions but are not definitive on the location of H+, present in some compounds. Theoretical calculations and Mass spectrometry will give the final answer.

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PS11.09.05 DIHYDRODIAZAPHOSPHININES IN THE SYNTHESIS OF MOLECULES OF BIOLOGICAL INTEREST.

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Dihydrodiazaphosphinines 1 have been firstly prepared at the University of Oviedo. We have studied their behavior against electrophiles,[1,2] particularly dimethylacetylenedicarboxylate (DMAD), by X-Ray diffraction and NMR Spectroscopy. This is another example of the *puzzlesome* chemistry unable to progress without structural information.

The reaction of 1 with DMAD at -20° C yield 2 as mayor product which shows a small C-C-C angle of 96.1° at the bridgehead carbon and a short C-C non-bonding distance of 228.05 pm. 2 is unstable and rearranges quantitatively to 3. Both 2 and 3 show similar structures to those of cocaine or atropine. With electrophiles, 2 reacts to policyclic compounds, 4, that co-crystallizes with a molecule of acid.

When 1 reacts with two equivalents of DMAD, a dihydrodiazaazulene system 5 is formed. Finally higher concentrations and even excesses of DMAD lead to the formation of 6.
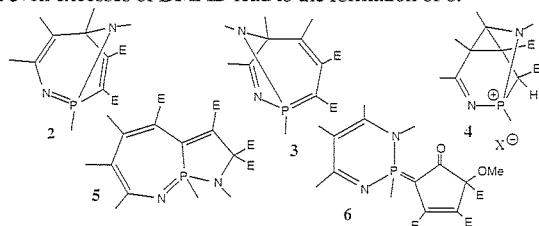
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PS11.09.06 STRUCTURAL VARIATIONS OF SODIUM PHENOLATE WITH DIFFERENT DONOR LIGANDS.

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Even though sodium phenolate has been applied industrially (Kolbe-Schmitt synthesis) since 1874, its crystal structure was still unknown. Recently, we succeeded in growing single crystals of solvent-free NaOPh, using a Bridgeman- Stockbarger-apparate. In the solid state, NaOPh forms polymeric one-dimensionals chains of dimeric units (Na_2O_2 rings), arranged along [001]. The coordination number of each Na atom is three. Remarkably, the Na atom also interacts with the neighboring phenyl ring (Na - C1 2.81(1) Na - C2 2.79(1)Å).

Sodium phenolate reacts with ethers (thf, 1,2-dimethoxyethane(dme)) with formation of tetrameric [Na(dme)OPh]$_4$ or hexameric [Na(thf)OPh]$_6$ units.

We believe that these studies will help to unterstand the reactivity of NaOPh towards CO_2 in the Kolbe-Schmitt synthesis.
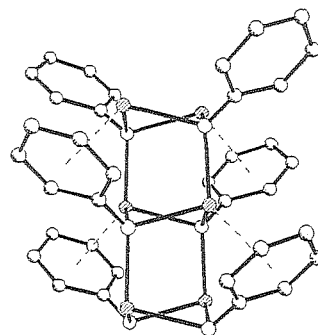

Figure 1 : Solid state structure of NaOPh

Other

PS11.10.01 THE IDEAL CRYSTAL AS A CRYTERION OF THE ACCURACY FOR THE APPROXIMATE EQUATIONS ON THE LIQUIDS.

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It is necessary for the statistical discription of collrctive effects in liquids to set that or other approximation between direct and pair correlation functions. Nowdays it is known about 20 approximate integral equations of the Ornsteine-Zernike (OZ) type connecting the direct and pair correlation fanctions. The degree of accuracy of every such approximation is impossible to be evaluated. The physical meaning of their basic approximations has not been cleared up to the end yet.

In our work we suggest using the generalized OZ equation for the discription of the ideal crystal. The pair correlation fanction in this limit case takes the meaning of the Dirak function. As a result, a linear integral equation for the direct correlation fanction is achieved, which has a simple analytical solution. It should fit the resalts known from crystallophysics for the ideal cristal. It is shown that in this limit case the neighbouring order disappear and the direct correlation function discribes a distant order which is typical for the ideal crystal. We suppose that the approximation correctly discribing of the limit tranzisition from the liqoid state to the solid state at T=0 will have the physics meaning. So the limit transition to the model of the ideal crystal may be considered as a physical criterion for the evaluation of the accuracy for the approximations used in physics of liquids.