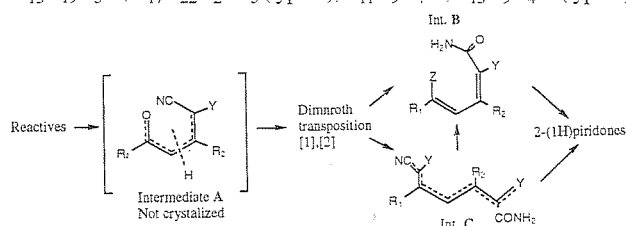


**PS11.09.04 REGIOSELECTIVE SYNTHESIS OF 2-(1H)PIRIDONES.** García-Rodríguez, E.<sup>(a)</sup>; García-Granda, S.<sup>(a)</sup>; Yustos Cuesta, P.<sup>(b)</sup>; Alberola Figueroa, A.<sup>(b)</sup>; González Ortega, A.<sup>(b)</sup>.  
 (a) Departamento de Química Física y Analítica. Universidad de Oviedo. Spain, (b) Departamento de Química Orgánica. Universidad de Valladolid. Spain

Piridones are relevant in the pharmacological industry and the studies of their synthetic 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<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>, C<sub>13</sub>H<sub>19</sub>N<sub>3</sub>O, C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>SO<sub>3</sub> (type B), C<sub>11</sub>H<sub>9</sub>N<sub>4</sub>O, C<sub>15</sub>H<sub>9</sub>N<sub>4</sub>O (type C).



(Z=–Pyrrolidine; Y=–CN, CO<sub>2</sub>Et, –SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>;  
 R<sub>1</sub>=Me, Et, iPr, Ph, ...; R<sub>2</sub>=H, Me, iPr, Ph, ...)

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

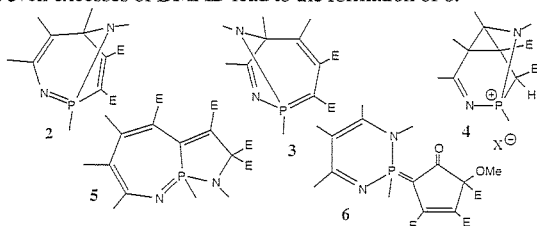
Wahnen, M. *Zeitschrift für Chemie* 9, 241-252 (1969)  
 Brennen, G., Schmidt, H. L. *Chem. Ber.* 110, 373, (1979)

**PS11.09.05 DIHYDRODIAZAPHOSPHININES IN THE SYNTHESIS OF MOLECULES OF BIOLOGICAL INTEREST.** A. Gutiérrez-Rodríguez<sup>a</sup>, R. Santiago-García<sup>a</sup>, S. García-Granda<sup>a</sup>, J. Barluenga<sup>b</sup>, M. Tomás<sup>b</sup>, K. Bieger<sup>b</sup>.  
 (a) Departamento de Química Física y Analítica. Universidad de Oviedo. 33071 Oviedo, Spain. (b) Instituto de Química Organometálica E. Moles

Dihydrodiazaphosphinines **1** have been firstly prepared at the University of Oviedo. We have studied their behavior against electrophiles,<sup>1,2</sup> 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 polycyclic compounds, **4**, that co-crystallizes with a molecule of acid.

When **1** reacts with two equivalents of DMAD, a dihydrodiazazulene system **5** is formed. Finally higher concentrations and even excesses of DMAD lead to the formation of **6**.



1. J. Barluenga; M. Tomás; K. Bieger; S. García-Granda; R. Santiago-García; *Angew. Chem. Int. Ed.* (Accepted for Publication).  
 2. S. García-Granda; R. Santiago-García; K. Bieger; *Acta Cryst. C* (Submitted).

**PS11.09.06 STRUCTURAL VARIATIONS OF SODIUM PHENOLATE WITH DIFFERENT DONOR LIGANDS.** J. Sielera<sup>a</sup>, M. Kunert<sup>b</sup>, E. Dinjus<sup>b</sup>.  
 a) Institut für Anorganische Chemie der Universität, D-04103 Leipzig, Linnestr. 3, b) Max-Planck-Gruppe für CO<sub>2</sub>-Chemie, D-07743 Jena, August-Bebel-Str.2

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-dimensional chains of dimeric units (Na<sub>2</sub>O<sub>2</sub> 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) Å - C2 2.79(1) Å).

Sodium phenolate reacts with ethers (thf, 1,2-dimethoxyethane(dme)) with formation of tetrameric [Na(dme)OPh]<sub>4</sub> or hexameric [Na(thf)OPh]<sub>6</sub> units.

We believe that these studies will help to understand the reactivity of NaOPh towards CO<sub>2</sub> in the Kolbe-Schmitt synthesis.

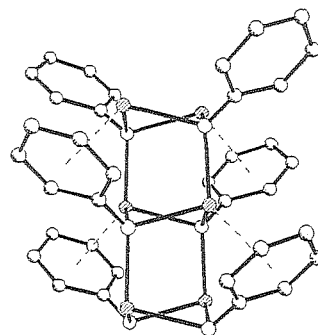


Figure 1 : Solid state structure of NaOPh

## Other

**PS11.10.01 THE IDEAL CRYSTAL AS A CRITERION OF THE ACCURACY FOR THE APPROXIMATE EQUATIONS ON THE LIQUIDS.** A.G. Balakchi and Yu.V. Agrafonov, Department of Physics, Irkutsk State University, 20 Gagarin Blvd., Irkutsk, 664003, Russia.

It is necessary for the statistical description of collective effects in liquids to set that or other approximation between direct and pair correlation functions. Nowadays it is known about 20 approximate integral equations of the Ornstein-Zernike (OZ) type connecting the direct and pair correlation functions. 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 description of the ideal crystal. The pair correlation function in this limit case takes the meaning of the Dirac function. As a result, a linear integral equation for the direct correlation function is achieved, which has a simple analytical solution. It should fit the results known from crystallophysics for the ideal crystal. It is shown that in this limit case the neighbouring order disappears and the direct correlation function describes a distant order which is typical for the ideal crystal. We suppose that the approximation correctly describing of the limit transition from the liquid 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.